Vol. XXVIII. [JUNE, 1906.] No. 6.

THE JOURNAL

OF THE

American Chemical Society

[CONTRIBUTION FROM THE U. S. DEPARTMENT OF AGRICULTURE, BUREAU OF CHEMISTRY. SENT BY H. W. WILEY.]

THE UNIFICATION OF REDUCING SUGAR METHODS.

BY L. S. MUNSON AND PERCY H. WALKER.

Received April 2, 1906.

SINCE Fehling[1] proposed the use of an alkaline copper tartrate solution for the quantitative estimation of reducing sugars, a large number of independent methods have been worked out having as their basis the power of these sugars to reduce such a copper solution. Among the most important and most generally used of these may be mentioned:

Allihn's method for *d*-glucose.[2]

Meissl's method for invert sugar alone, and in the presence of amounts of sucrose varying between 90 and 99 per cent.[3]

Hiller's method for invert sugar in presence of less than 90 per cent. sucrose.[4]

Herzfeld's method for 1 per cent. or less of invert sugar and a high percentage of sucrose.[5]

Soxhlet's method for lactose.[6]

Soxhlet's method for maltose.[7]

[1] Ann. 72, 106.

[2] J. pr. Chem. 22, 46 (1880).

[3] Z. Ver. Rübenzucker Ind. 29, 1034 (1879).

[4] Ibid. 39, 734 (1889).

[5] Ibid. 35, 985 (1885).

[6] J. pr. Chem. 21, 227 (1880).

[7] Allg. Brau. Hopf. Ztg., 1885.

Brown, Morris and Millar's method for *d*-glucose,[1] δ-fructose and invert sugar.[2]

Kjeldahl's method for *d*-glucose, δ-fructose, invert sugar maltose, lactose and galactose.[3]

Defren's method for *d*-glucose, maltose and lactose.[4]

In all of the above methods the copper sulphate solution used has remained practically identical, *viz.*, 34.639 grams crystallized copper sulphate in 500 cc., which is very nearly the same concentration as was suggested by Fehling in 1850. The alkaline tartrate solutions and the methods of manipulation employed by the different analysts, however, have varied materially and as both of these factors have a marked effect upon the copper reducing powers of the different sugars, these variations constitute the principal differences in the methods above mentioned.

This work upon reducing sugars was taken up, therefore, for the purpose of so unifying the methods of analysis that a single set of solutions and a common method of manipulation might be used for all reducing sugars. This necessitated a consideration of the solutions to be employed with reference to their effect upon non-reducing sugars when present; the time required for making the determination; the accuracy and simplicity of the method, and the most satisfactory manner of conducting the reduction. It was also necessary that due consideration be given to methods that had long been in use, and consequently radical change from which might be made with reluctance.

The solutions of copper sulphate and of alkaline tartrate, commonly known as Soxhlet's solutions, were accepted as the most satisfactory for general use and these solutions have probably been more generally used in the past than any other set. Besides, these solutions are the ones employed almost exclusively, in this country at least, for volumetric work.

In the manner of making the reductions, two widely different general methods have been employed. Almost invariably the older workers have employed direct boiling for a short period, while the later workers, Brown, Morris and Millar, Kjeldahl, and

[1] The name which is accepted by international scientific usage is employed throughout this paper in place of "dextrose," which is more commonly used in American technical literature.

[2] J. Chem. Soc. 71, 275 (1897).

[3] Compt. rend. des travaux du laboratoire de Carlsberg, 1895, p. 1.

[4] This Journal, 18, 749 (1896).

Defren, have employed heating in a boiling water-bath, conducting the reduction for a longer period than where direct boiling is practised. Kjeldahl, in addition, made the reduction in an atmosphere of hydrogen, thus avoiding the effect of atmospheric oxidation, but this precaution makes the method too cumbersome to permit of its general use. In reference to the manner of conducting the reduction, advantages seemed to be largely in favor of direct boiling for a short period. In an investigation of this subject by one of us[1] it was shown that while somewhat higher results were obtained by heating in boiling water for a long period, the reduction even at the end of fifteen minutes was far from complete and that chances of surface oxidation were much greater than by direct boiling. The method of boiling over a free flame was therefore accepted.

PREPARATION OF SOLUTIONS AND METHOD OF MANIPULATION.

Copper sulphate solution must contain 34.639 grams of crystallized copper sulphate of highest purity in 500 cc. This salt should contain not more than mere traces of iron.

Alkaline tartrate solution must contain 173 grams of Rochelle salt and 50 grams of sodium hydroxide in 500 cc. The amount of alkali to be used is best obtained by weighing out a concentrated solution of sodium hydroxide, the strength of which has been determined by titration. It is not considered essential that this solution be prepared fresh each day, as many workers recommend. In case any precipitate separates out this is filtered off before using; otherwise our experience has been that this solution undergoes no material change upon standing for reasonable lengths of time.

Manipulation.—Transfer 25 cc. each of the copper and alkaline tartrate solutions to a 400 cc. Jena or Non-sol beaker and add 50 cc. of reducing sugar solution, or, if a smaller volume of sugar solution be used, add water to make the final volume 100 cc. Heat the beaker upon an asbestos gauze over a Bunsen burner, so regulate the flame that boiling begins in four minutes, and continue the boiling for exactly two minutes. Keep the beaker covered with a watch-glass throughout the entire time of heating. Without diluting, filter the cuprous oxide at once on an asbestos felt in a porcelain Gooch crucible, using suction. Wash the

[1] Proc. A. O. A. C., Bur. Chem., Bull. 73, p. 59.

cuprous oxide thoroughly with water at a temperature of about 60° C., then with 10 cc. of alcohol and finally with 10 cc. of ether. Dry for thirty minutes in a water oven at 100°, cool in a desiccator and weigh as cuprous oxide.

Direct Weighing of Cuprous Oxide.—This method of determining copper has been practised in the laboratories of the Bureau of Chemistry for a number of years and has given most excellent results. The method was checked several years ago[1] against the electrolytic method and later against Low's thiosulphate method as described in this Journal, **24,** 1082 (1902), and the accuracy of the cuprous oxide method demonstrated.[2]

It is by far the most convenient method for the copper determination, the only precaution necessary in its use being the preparation of the asbestos. It has been the custom here to prepare the asbestos, which should be the amphibole variety, by first digesting with 1:3 hydrochloric acid for two or three days. Wash free from acid and digest for a similar period with soda solution, after which treat for a few hours with hot alkaline copper tartrate solution of the strength employed in sugar determinations. The asbestos is then washed free from alkali, finally digested with nitric acid for several hours, and after washing free from acid it is shaken up with water for use. In preparing the Gooch crucible load it with a film of asbestos one-fourth inch thick, wash this thoroughly with water to remove fine particles of asbestos; finally wash with alcohol and ether, dry for thirty minutes at 100°, cool in a desiccator and weigh.

It has been found most convenient to dissolve the cuprous oxide each time after weighing, with nitric acid, and use the same felts over and over again, as they improve with use. Twenty-

[1] Proc. A. O. A. C., Bur. Chem., Bull. 73, p. 59.

[2] For pure *d*-glucose and invert sugar the copper contained in the cuprous oxide corresponds within the limits of experimental error to the theoretical amount. The same is true with the mixture of invert sugar and sucrose when 400 milligrams of total sugar are used. For the mixture containing two grams total sugar, the copper content of the precipitate is slightly lower than theory indicates but the variation is not great enough to affect the results; besides, the results recorded are based on the weights of the precipitate and not on the content of copper. When as much as 10 grams total sugar are used, the variation from the theory may amount to several milligrams, but this variation is constant and would introduce no error when working with tables based on direct weighing of cuprous oxide.

six crucibles were thus used throughout this work and the average loss for an average of seventeen determinations with each crucible was but 0.39 mg. each determination. This loss is partly mechanical and results partly from the solvent action of the reagents used.

Spontaneous Precipitation of Cuprous Oxide.—When alkaline copper tartrate is boiled, a slight spontaneous precipitation of cuprous oxide takes place and the regular determinations should be corrected by the amount of cuprous oxide thus precipitated. In this work each one of us ran two blanks each day that determinations were made and the results of each worker are corrected by his blanks for that day. In this way proper correction is made for the cuprous oxide precipitated spontaneously as well as for any loss of asbestos, through solvent action of the alkaline liquid.

The following table shows the blanks obtained throughout this investigation. Attention is called to the rather wide range shown by some of these blanks.

Working in the manner above described the copper-reducing power of *d*-glucose, invert sugar, and two mixtures of invert sugar and sucrose was determined. All weights of sugar and of cuprous oxide are expressed in terms of brass weights in air. The flasks and pipettes used were accurately graduated by the Bureau of Standards and all were very close to their indicated volumes. In no case was the error introduced by their use sufficient to take into consideration.

Pure *d*-glucose was prepared by repeatedly recrystallizing the commercial product. The material finally used showed for $(\alpha)_D^{20}$ a value of 53.17, with a concentration of 20 per cent., which value corresponds very closely to that calculated according to Tollen's formula.

Pure sucrose was prepared according to the method prescribed by the International Commission for Unifying Methods of Sugar Analysis, and the product used was shown to be of the highest purity. Invert sugar was prepared from this sucrose by hydrolyzing with fifth-normal hydrochloric acid, using 10 cc. of this acid for each 100 cc. final volume of invert sugar solution and heating upon the steam-bath for thirty minutes. The solution was then cooled rapidly, the acid barely neutralized with fifth-normal sodium hydroxide, and the volume completed at the

TABLE I.

Number of set.	Individual blanks. Munson. Mgs.	Individual blanks. Walker. Mgs.	Average. Munson. Mgs.	Average. Walker. Mgs.
1	0.4	1.4		
	—0.4	0.2	0.0	0.8
2	1.0	—0.6		
	—0.7	0.5	0.1	0.0
3	0.5	0.0		
	0.2	0.0	0.3	0.0
4	0.0	—0.4		
	—0.6	0.2	—0.3	—0.1
5	0.4	—0.4		
	—0.4	0.0	0.0	—0.2
6	1.6	0.8		
	0.5	—0.5	1.0	0.1
7	0.3	0.2		
	0.3	0.6	0.3	0.4
8	0.8	...		
	—0.2	0.6	0.3	0.6
9	0.3	0.2		
	0.8	0.6	0.5	0.4
10	0.6	0.4		
	0.4	2.0	0.5	1.2
11	—0.5	1.0		
	—0.5	1.6	—0.5	1.3
12	1.3	0.4		
	0.8	0.8	1.1	0.6
13	0.9	1.0		
	0.5	0.6	0.7	0.8
14	0.5	0.1		
	0.3	—0.4	0.4	—0.2
15	—0.4	0.1		
	0.2	1.0	—0.1	0.5
16	0.0	0.0		
	—0.1	0.0	0.0	0.0
17	—0.3	—1.3		
	—0.1	—1.0	—0.2	—1.2

temperature of graduation of the flask. Care was taken to retain this temperature until all portions were measured out. In all cases at least two different solutions were used in establishing each point and duplicate determinations were made by each worker. Points were determined 20 mgs. apart, beginning with 20 mgs. for each of the sugars and mixtures. With the invert sugar and sucrose mixtures, the requisite amount of cane-sugar was obtained by measuring with a burette a sucrose solution of known concentration. Results of all determinations for the four series are given in Table II. From the averages for each series a curve was drawn upon cross-section paper and by use of these curves the individual determinations that were sufficiently far from the curve to be considered among the less accurate of the determinations made were eliminated from the final averages. While all determinations made for each point are recorded, greatest weight was given to those lying nearest the curve. Those determinations not included in final averages are indicated by a star.

When working with either *d*-glucose or invert sugar alone, the results obtained were very uniform and agreed within reasonable limits of experimental error. With the mixtures of invert sugar and sucrose, however, results were less uniform, especially where large amounts of sucrose were present. Two sugar mixtures were worked upon, one containing a total of 0.400 gram invert sugar and sucrose and the other a total of 2,000 grams. By reference to the tables it is seen that the presence of sucrose materially increases the reduction, the amount of increase being influenced primarily by the amount of sucrose present and secondarily by the amount of invert sugar present. The amount of sucrose remaining the same, its influence will be less when a large amount of reducing sugar is present than when only a small amount is present.

In using a definite amount of total sugar, the authors have followed the plan carried out by Herzfeld in his method of determining 1 per cent. or less of invert sugar in the presence of large amounts of sucrose, and it is believed that this method of procedure will give much more satisfactory results with a less amount of analytical work than does the method of Meissl and Hiller, upon the basis of which tables have been worked out for definite percentages of invert sugar and sucrose.

From each series of average results as given in Table II was deduced, according to the method of least squares, the formula for calculating reducing sugar from any weight of cuprous oxide within limits of the method. In these formulas y=cuprous oxide and x=reducing sugar.

For *d*-glucose,

$$y=0.5614+2.3484\ x-0.001209\ x^2.$$

For invert sugar alone,

$$y=-0.2460+2.2747\ x-0.001077\ x^2.$$

For invert sugar and sucrose, 0.400 gram total,

$$y=6.3886+2.2279\ x-0.0009703\ x^2.$$

For invert sugar and sucrose, 2.000 grams total,

$$y=20.6600+2.2021\ x-0.0009030\ x^2.$$

From these formulas the points of each series corresponding to the determined points were calculated, and in Table III are given the determined and the calculated values of each series together with the differences between these values. With dextrose, invert sugar, and the invert sugar and sucrose mixture of 0.400 gram total, these differences are very small and negligible. The 2,000 grams mixture showed less concordance, although satisfactory results were obtained.

Table IV gives the sugar values for each series of reducing sugars for each milligram of cuprous oxide between 10 and 490. The values for points 10 milligrams apart, beginning with 10 milligrams of cuprous oxide, were calculated from the formula and all intermediate points were determined by interpolation. The copper equivalents of cuprous oxide given in the second column of this table were obtained by multiplying cuprous oxide by 0.88827.

When this work was taken up it was hoped that factors might be worked out for all of the more important reducing sugars and for such mixtures as seemed necessary. To date, however, only the factors for *d*-glucose, invert sugar and two mixtures of invert sugar and sucrose have been determined. In continuing this investigation it will be necessary to do further work on other invert sugar and sucrose mixtures. Maltose and lactose are other important reducing sugars for which the present methods of determination are not entirely satisfactory, and the authors hope to take up the work on these within the next few months.

TABLE II.

Reducing sugar. Mgs.	*d*-Glucose. Weight of Cu_2O. Munson. Mgs.	*d*-Glucose. Weight of Cu_2O. Walker. Mgs.	*d*-Glucose. Average result. Mgs.	Invert sugar. Weight of Cu_2O. Munson. Mgs.	Invert sugar. Weight of Cu_2O. Walker. Mgs.	Invert sugar. Average result. Mgs.	Invert sugar and sucrose —0.400 gram total. Weight of Cu_2O. Munson. Mgs.	Invert sugar and sucrose —0.400 gram total. Weight of Cu_2O. Walker. Mgs.	Invert sugar and sucrose —0.400 gram total. Average result. Mgs.	Invert sugar and sucrose —2.0000 grams total. Weight of Cu_2O. Munson. Mgs.	Invert sugar and sucrose —2.0000 grams total. Weight of Cu_2O. Walker. Mgs.	Invert sugar and sucrose —2.0000 grams total. Average result. Mgs.
20	46.7	47.4	47.1	44.5	44.8	44.9	49.0*	50.5	50.4	64.8	66.2	64.5
	46.3	47.8	...	45.3	44.8	...	50.5	50.1	...	62.3	62.5	...
	...	...	...	...	...	...	...	...	...	65.8	65.4	...
	...	...	...	...	...	...	...	...	...	65.2	68.7*	...
40	92.6	92.2	92.6	88.7	89.8	89.0	95.1	93.9	94.9	108.0	105.9	106.7
	...	93.1	...	89.1	88.2	...	95.1	95.4	...	105.6	107.4	...
60	136.3	137.2	137.0	131.9	131.6	132.3	136.2	136.7	135.9	150.1	148.1	149.1
	137.6	136.8	...	132.7	132.8	...	134.1*	135.5	...	149.5	148.8	...
	...	...	...	...	...	...	135.0	134.0*	...	...	...	...
80	180.8	180.4	180.6	175.1	174.8	174.9	178.8	180.3*	178.0	193.4	193.4	193.0
	179.9	181.4	...	174.9	176.6*	...	178.8	180.6*	...	191.4	193.7	...
	...	...	...	...	...	...	177.8	178.7	...	...	...	...
	...	...	...	...	...	...	176.6	177.0	...	...	...	...
100	224.1	223.5	223.7	218.0*	215.9	216.7	216.9*	218.9	219.4	230.1	229.8	230.7
	224.1	223.1	...	217.1	217.2	...	214.9*	219.5	..	232.0	231.0	...
	...	...	...	....	...	...	219.9	219.4	...	...	...	...
	...	...	...	...	...	...	219.4	219.5	...	...	...	...
120	265.3	263.7	264.9	257.0	257.4	257.0	256.1*	258.1	259.6	271.0	271.7	272.3
	265.0	265.8	...	256.1	259.0	...	260.5	260.6	...	271.2	273.8	...
	265.7	264.0	...	255.9	258.0	...	258.0	260.7	...	273.9	274.8*	...
	...	...	...	257.1	258.2	...	258.5	260.3	...	272.3	276.9*	...
	...	...	...	255.7	255.0*	...	260.0	...	...	...	...	...
	...	...	...	255.6	256.5	...	...	...	...	...	...	...

TABLE II—*Continued.*

Reducing sugar. Mgs.	*d*-Glucose. Weight of Cu_2O. Munson. Mgs.	*d*-Glucose. Weight of Cu_2O. Walker. Mgs.	*d*-Glucose. Average result. Mgs.	Invert sugar. Weight of Cu_2O. Munson. Mgs.	Invert sugar. Weight of Cu_2O. Walker. Mgs.	Invert sugar. Average result. Mgs.	Invert sugar and sucrose —0.400 gram total. Weight of Cu_2O. Munson. Mgs.	Invert sugar and sucrose —0.400 gram total. Weight of Cu_2O. Walker. Mgs.	Invert sugar and sucrose —0.400 gram total. Average result. Mgs.	Invert sugar and sucrose —2.0000 grams total. Weight of Cu_2O. Munson. mgs.	Invert sugar and sucrose —2.0000 grams total. Weight of Cu_2O. Walker. Mgs.	Invert sugar and sucrose —2.0000 grams total. Average result. Mgs.
140	305.1	305.2	305.2	296.9	297.2	297.3	300.2	299.5	300.0	310.8	311.2	311.2
	305.2	305.2	...	297.0	298.2	...	299.7	300.5	...	310.6	312.2	...
160	343.8*	345.7	345.2	334.8	335.0	335.1	337.4	337.6	337.9	347.7*	349.4	349.4
	345.0	345.5	...	335.5	335.2	...	337.4	339.2	...	348.9	349.8	...
	344.9	344.7	...	...	...	...	...	337.7	...	...	...	...
180	384.7	383.7	384.3	370.0*	375.2	374.6	375.0	375.7	375.5	388.8	388.4	388.6
	385.1	383.7	...	373.8	374.2	...	373.9*	376.0	...	388.7	388.6	...
	...	...	...	374.9	374.8	...	374.5	376.4	...	...	...	...
	...	...	...	...	...	...	374.9	375.4	...	...	...	...
	...	...	...	...	...	...	...	375.9	...	...	...	...
200	422.1	421.5	421.7	411.8	411.6	411.4	413.5	414.2	413.7	422.6	424.0	423.6
	421.3	421.7	...	410.9	411.4	...	412.8	414.4	...	423.2	424.4	...
220	459.0	460.5	459.8	449.0	450.5*	449.1	450.4	449.6	449.8	461.9	462.4	462.2
	459.5	460.2	...	449.0	449.4	...	448.7	450.6	...	463.2	461.2	...
240	493.9	493.8	493.8	482.5	483.7	483.1	481.7*	484.4	484.8	...	...	...
	493.5	494.0	...	483.1	483.2	...	483.2*	484.4	...	...	...	...
	...	...	...	...	...	...	485.0	485.3	...	...	...	...

TABLE III.

Reducing sugar. Mgs.	*d*-Glucose. Determined Cu_2O. Mgs.	*d*-Glucose. Calculated Cu_2O. Mgs.	*d*-Glucose. Difference. Mgs.	Invert sugar. Determined Cu_2O. Mgs.	Invert sugar. Calculated Cu_2O. Mgs.	Invert sugar. Difference. Mgs.	Invert sugar and sucrose —0.400 gram total. Determined Cu_2O. Mgs.	Invert sugar and sucrose —0.400 gram total. Calculated Cu_2O. Mgs.	Invert sugar and sucrose —0.400 gram total. Difference. Mg.	Invert sugar and sucrose —2.0000 grams total. Determined Cu_2O. Mgs.	Invert sugar and sucrose —2.0000 grams total. Calculated Cu_2O. Mgs.	Invert sugar and sucrose —2.0000 grams total. Difference. Mgs.
20	47.1	47.0	0.1	44.9	44.8	0.1	50.4	50.6	—0.2	64.5	64.3	0.2
40	92.6	92.6	0.0	89.0	89.0	0.0	94.9	94.0	0.9	106.7	107.3	—0.6
60	137.0	137.1	—0.1	132.3	132.5	—0.2	135.9	136.6	—0.7	149.1	149.5	—0.4
80	180.6	180.7	—0.1	174.9	174.9	0.0	178.0	178.4	—0.4	193.0	191.1	1.9
100	223.7	223.3	0.4	216.7	216.4	0.3	219.4	219.5	—0.1	230.7	231.8	—1.1
120	264.9	265.0	—0.1	257.0	257.2	—0.2	259.6	259.8	—0.2	272.3	271.9	0.4
140	305.2	305.6	—0.4	297.3	297.1	0.2	300.0	299.3	0.7	311.2	311.3	—0.1
160	345.2	345.4	—0.2	335.1	336.1	—1.0	337.9	338.0	—0.1	349.4	349.9	—0.5
180	384.3	384.1	0.2	374.6	374.3	0.3	375.5	376.0	—0.5	388.6	387.8	0.8
200	421.7	421.9	—0.2	411.4	411.6	—0.2	413.7	413.2	0.5	423.6	425.0	—1.4
220	459.8	458.7	1.1	449.1	448.0	1.1	449.8	449.6	0.2	462.2	461.4	0.8
240	493.8	494.5	—0.7	483.1	483.6	—0.5	484.8	485.2	—0.4	...	...	...
		Aver.	0.30			0.34			0.41			0.75

TABLE IV.

Cuprous oxide (Cu_2O). Mgs.	Copper (Cu). Mgs.	*d*-Glucose. Mgs.	Invert sugar. Mgs.	Invert sugar and sucrose. 0.400 gram. Total mgs.	Invert sugar and sucrose. 2.0000 grams. Total mgs.
10	8.9	4.0	4.5	1.6	
11	9.8	4.5	5.0	2.1	
12	10.7	4.9	5.4	2.5	
13	11.5	5.3	5.8	3.0	
14	12.4	5.7	6.3	3.4	
15	13.3	6.2	6.7	3.9	
16	14.2	6.6	7.2	4.3	
17	15.1	7.0	7.6	4.8	
18	16.0	7.5	8.1	5.2	
19	16.9	7.9	8.5	5.7	
20	17.8	8.3	8.9	6.1	
21	18.7	8.7	9.4	6.6	
22	19.5	9.2	9.8	7.0	
23	20.4	9.6	10.3	7.5	
24	21.3	10.0	10.7	7.9	
25	22.2	10.5	11.2	8.4	
26	23.1	10.9	11.6	8.8	
27	24.0	11.3	12.0	9.3	
28	24.9	11.8	12.5	9.7	
29	25.8	12.2	12.9	10.2	
30	26.6	12.6	13.4	10.7	4.3
31	27.5	13.1	13.8	11.1	4.7
32	28.4	13.5	14.3	11.6	5.2
33	29.3	13.9	14.7	12.0	5.6
34	30.2	14.3	15.2	12.5	6.1
35	31.1	14.8	15.6	12.9	6.5
36	32.0	15.2	16.1	13.4	7.0
37	32.9	15.6	16.5	13.8	7.4
38	33.8	16.1	16.9	14.3	7.9
39	34.6	16.5	17.4	14.7	8.4
40	35.5	16.9	17.8	15.2	8.8
41	36.4	17.4	18.3	15.6	9.3
42	37.3	17.8	18.7	16.1	9.7
43	38.2	18.2	19.2	16.6	10.2
44	39.1	18.7	19.6	17.0	10.7
45	40.0	19.1	20.1	17.5	11.1
46	40.9	19.6	20.5	17.9	11.6
47	41.7	20.0	21.0	18.4	12.0

TABLE IV—*Continued.*

Cuprous oxide (Cu_2O). Mgs.	Copper (Cu). Mgs.	*d*-Glucose. Mgs.	Invert sugar. Mgs.	Invert sugar and sucrose. 0.400 gram. Total mgs.	Invert sugar and sucrose. 2.0000 grams. Total mgs.
48	42.6	20.4	21.4	18.8	12.5
49	43.5	20.9	21.9	19.3	12.9
50	44.4	21.3	22.3	19.7	13.4
51	45.3	21.7	22.8	20.2	13.9
52	46.2	22.2	23.2	20.7	14.3
53	47.1	22.6	23.7	21.1	14.8
54	48.0	23.0	24.1	21.6	15.2
55	48.9	23.5	24.6	22.0	15.7
56	49.7	23.9	25.0	22.5	16.2
57	50.6	24.3	25.5	22.9	16.6
58	51.5	24.8	25.9	23.4	17.1
59	52.4	25.2	26.4	23.9	17.5
60	53.3	25.6	26.8	24.3	18.0
61	54.2	26.1	27.3	24.8	18.5
62	55.1	26.5	27.7	25.2	18.9
63	56.0	27.0	28.2	25.7	19.4
64	56.8	27.4	28.6	26.2	19.8
65	57.7	27.8	29.1	26.6	20.3
66	58.6	28.3	29.5	27.1	20.8
67	59.5	28.7	30.0	27.5	21.2
68	60.4	29.2	30.4	28.0	21.7
69	61.3	29.6	30.9	28.5	22.2
70	62.2	30.0	31.3	28.9	22.6
71	63.1	30.5	31.8	29.4	23.1
72	64.0	30.9	32.3	29.8	23.5
73	64.8	31.4	32.7	30.3	24.0
74	65.7	31.8	33.2	30.8	24.5
75	66.6	32.2	33.6	31.2	24.9
76	67.5	32.7	34.1	31.7	25.4
77	68.4	33.1	34.5	32.1	25.9
78	69.3	33.6	35.0	32.6	26.3
79	70.2	34.0	35.4	33.1	26.8
80	71.1	34.4	35.9	33.5	27.3
81	71.9	34.9	36.3	34.0	27.7
82	72.8	35.3	36.8	34.5	28.2
83	73.7	35.8	37.3	34.9	28.6
84	74.6	36.2	37.7	35.4	29.1

TABLE IV—*Continued.*

Cuprous oxide (Cu_2O). Mgs.	Copper (Cu). Mgs.	*d*-Glucose. Mgs.	Invert sugar. Mgs.	Invert sugar and sucrose. 0.400 gram. Total mgs.	Invert sugar and sucrose. 2.0000 grams. Total mgs.
85	75.5	36.7	38.2	35.8	29.6
86	76.4	37.1	38.6	36.3	30.0
87	77.3	37.5	39.1	36.8	30.5
88	78.2	38.0	39.5	37.2	31.0
89	79.1	38.4	40.0	37.7	31.4
90	79.9	38.9	40.4	38.2	31.9
91	80.8	39.3	40.9	38.6	32.4
92	81.7	39.8	41.4	39.1	32.8
93	82.6	40.2	41.8	39.6	33.3
94	83.5	40.6	42.3	40.0	33.8
95	84.4	41.1	42.7	40.5	34.2
96	85.3	41.5	43.2	41.0	34.7
97	86.2	42.0	43.7	41.4	35.2
98	87.1	42.4	44.1	41.9	35.6
99	87.9	42.9	44.6	42.4	36.1
100	88.8	43.3	45.0	42.8	36.6
101	89.7	43.8	45.5	43.3	37.0
102	90.6	44.2	46.0	43.8	37.5
103	91.5	44.7	46.4	44.2	38.0
104	92.4	45.1	46.9	44.7	38.5
105	93.3	45.5	47.3	45.2	38.9
106	94.2	46.0	47.8	45.6	39.4
107	95.0	46.4	48.3	46.1	39.9
108	95.9	46.9	48.7	46.6	40.3
109	96.8	47.3	49.2	47.0	40.8
110	97.7	47.8	49.6	47.5	41.3
111	98.6	48.2	50.1	48.0	41.7
112	99.5	48.7	50.6	48.4	42.2
113	100.4	49.1	51.0	48.9	42.7
114	101.3	49.6	51.5	49.4	43.2
115	102.2	50.0	51.9	49.8	43.6
116	103.0	50.5	52.4	50.3	44.1
117	103.9	50.9	52.9	50.8	44.6
118	104.8	51.4	53.3	51.2	45.0
119	105.7	51.8	53.8	51.7	45.5
120	106.6	52.3	54.3	52.2	46.0
121	107.5	52.7	54.7	52.7	46.5

TABLE IV—*Continued.*

Cuprous oxide (Cu_2O). Mgs.	Copper (Cu). Mgs.	*d*-Glucose. Mgs.	Invert sugar. Mgs.	Invert sugar and sucrose. 0.400 gram. Total mgs.	Invert sugar and sucrose. 2.0000 grams. Total mgs.
122	108.4	53.2	55.2	53.1	46.9
123	109.3	53.6	55.7	53.6	47.4
124	110.1	54.1	56.1	54.1	47.9
125	111.0	54.5	56.6	54.5	48.3
126	111.9	55.0	57.0	55.0	48.8
127	112.8	55.4	57.5	55.5	49.3
128	113.7	55.9	58.0	55.9	49.8
129	114.6	56.3	58.4	56.4	50.2
130	115.5	56.8	58.9	56.9	50.7
131	116.4	57.2	59.4	57.4	51.2
132	117.3	57.7	59.8	57.8	51.7
133	118.1	58.1	60.3	58.3	52.1
134	119.0	58.6	60.8	58.8	52.6
135	119.9	59.0	61.2	59.3	53.1
136	120.8	59.5	61.7	59.7	53.6
137	121.7	60.0	62.2	60.2	54.0
138	122.6	60.4	62.6	60.7	54.5
139	123.5	60.9	63.1	61.2	55.0
140	124.4	61.3	63.6	61.6	55.5
141	125.2	61.8	64.0	62.1	55.9
142	126.1	62.2	64.5	62.6	56.4
143	127.0	62.7	65.0	63.1	56.9
144	127.9	63.1	65.4	63.5	57.4
145	128.8	63.6	65.9	64.0	57.8
146	129.7	64.0	66.4	64.5	58.3
147	130.6	64.5	66.9	65.0	58.8
148	131.5	65.0	67.3	65.4	59.3
149	132.4	65.4	67.8	65.9	59.7
150	133.2	65.9	68.3	66.4	60.2
151	134.1	66.3	68.7	66.9	60.7
152	135.0	66.8	69.2	67.3	61.2
153	135.9	67.2	69.7	67.8	61.7
154	136.8	67.7	70.1	68.3	62.1
155	137.7	68.2	70.6	68.8	62.6
156	138.6	68.6	71.1	69.2	63.1
157	139.5	69.1	71.6	69.7	63.6
158	140.3	69.5	72.0	70.2	64.1

TABLE IV—*Continued.*

Cuprous oxide (Cu_2O). Mgs.	Copper (Cu). Mgs.	*d*-Glucose. Mgs.	Invert sugar. Mgs.	Invert sugar and sucrose. 0.400 gram. Total mgs.	Invert sugar and sucrose. 2.0000 grams. Total mgs.
159	141.2	70.0	72.5	70.7	64.5
160	142.1	70.4	73.0	71.2	65.0
161	143.0	70.9	73.4	71.6	65.5
162	143.9	71.4	73.9	72.1	66.0
163	144.8	71.8	74.4	72.6	66.5
164	145.7	72.3	74.9	73.1	66.9
165	146.6	72.8	75.3	73.6	67.4
166	147.5	73.2	75.8	74.0	67.9
167	148.3	73.7	76.3	74.5	68.4
168	149.2	74.1	76.8	75.0	68.9
169	150.1	74.6	77.2	75.5	69.3
170	151.0	75.1	77.7	76.0	69.8
171	151.9	75.5	78.2	76.4	70.3
172	152.8	76.0	78.7	76.9	70.8
173	153.7	76.4	79.1	77.4	71.3
174	154.6	76.9	79.6	77.9	71.7
175	155.5	77.4	80.1	78.4	72.2
176	156.3	77.8	80.6	78.8	72.7
177	157.2	78.3	81.0	79.3	73.2
178	158.1	78.8	81.5	79.8	73.7
179	159.0	79.2	82.0	80.3	74.2
180	159.9	79.7	82.5	80.8	74.6
181	160.8	80.1	82.9	81.3	75.1
182	161.7	80.6	83.4	81.7	75.6
183	162.6	81.1	83.9	82.2	76.1
184	163.4	81.5	84.4	82.7	76.6
185	164.3	82.0	84.9	83.2	77.1
186	165.2	82.5	85.3	83.7	77.6
187	166.1	82.9	85.8	84.2	78.0
188	167.0	83.4	86.3	84.6	78.5
189	167.9	83.9	86.8	85.1	79.0
190	168.8	84.3	87.2	85.6	79.5
191	169.7	84.8	87.7	86.1	80.0
192	170.5	85.3	88.2	86.6	80.5
193	171.4	85.7	88.7	87.1	81.0
194	172.3	86.2	89.2	87.6	81.4

TABLE IV—*Continued.*

Cuprous oxide (Cu_2O). Mgs.	Copper (Cu). Mgs.	*d*-Glucose. Mgs.	Invert sugar. Mgs.	Invert sugar and sucrose. 0.400 gram. Total mgs.	Invert sugar and sucrose. 2.0000 grams. Total mgs.
195	173.2	86.7	89.6	88.0	81.9
196	174.1	87.1	90.1	88.5	82.4
197	175.0	87.6	90.6	89.0	82.9
198	175.9	88.1	91.1	89.5	83.4
199	176.8	88.5	91.6	90.0	83.9
200	177.7	89.0	92.0	90.5	84.4
201	178.5	89.5	92.5	91.0	84.8
202	179.4	89.9	93.0	91.4	85.3
203	180.3	90.4	93.5	91.9	85.8
204	181.2	90.9	94.0	92.4	86.3
205	182.1	91.4	94.5	92.9	86.8
206	183.0	91.8	94.9	93.4	87.3
207	183.9	92.3	95.4	93.9	87.8
208	184.8	92.8	95.9	94.4	88.3
209	185.6	93.2	96.4	94.9	88.8
210	186.5	93.7	96.9	95.4	89.2
211	187.4	94.2	97.4	95.8	89.7
212	188.3	94.6	97.8	96.3	90.2
213	189.2	95.1	98.3	96.8	90.7
214	190.1	95.6	98.8	97.3	91.2
215	191.0	96.1	99.3	97.8	91.7
216	191.9	96.5	99.8	98.3	92.2
217	192.8	97.0	100.3	98.8	92.7
218	193.6	97.5	100.8	99.3	93.2
219	194.5	98.0	101.2	99.8	93.7
220	195.4	98.4	101.7	100.3	94.2
221	196.3	98.9	102.2	100.8	94.7
222	197.2	99.4	102.7	101.2	95.1
223	198.1	99.9	103.2	101.7	95.6
224	199.0	100.3	103.7	102.2	96.1
225	199.9	100.8	104.2	102.7	96.6
226	200.7	101.3	104.6	103.2	97.1
227	201.6	101.8	105.1	103.7	97.6
228	202.5	102.2	105.6	104.2	98.1
229	203.4	102.7	106.1	104.7	98.6
230	204.3	103.2	106.6	105.2	99.1
231	205.2	103.7	107.1	105.7	99.6

TABLE IV—*Continued.*

Cuprous oxide (Cu_2O). Mgs.	Copper (Cu). Mgs.	*d*-Glucose. Mgs.	Invert sugar. Mgs.	Invert sugar and sucrose. 0.400 gram. Total mgs.	Invert sugar and sucrose. 2.0000 grams. Total mgs.
232	206.1	104.1	107.6	106.2	100.1
233	207.0	104.6	108.1	106.7	100.6
234	207.9	105.1	108.6	107.2	101.1
235	208.7	105.6	109.1	107.7	101.6
236	209.6	106.0	109.5	108.2	102.1
237	210.5	106.5	110.0	108.7	102.6
238	211.4	107.0	110.5	109.2	103.1
239	212.3	107.5	111.0	109.6	103.5
240	213.2	108.0	111.5	110.1	104.0
241	214.1	108.4	112.0	110.6	104.5
242	215.0	108.9	112.5	111.1	105.0
243	215.8	109.4	113.0	111.6	105.5
244	216.7	109.9	113.5	112.1	106.0
245	217.6	110.4	114.0	112.6	106.5
246	218.5	110.8	114.5	113.1	107.0
247	219.4	111.3	115.0	113.6	107.5
248	220.3	111.8	115.4	114.1	108.0
249	221.2	112.3	115.9	114.6	108.5
250	222.1	112.8	116.4	115.1	109.0
251	223.0	113.2	116.9	115.6	109.5
252	223.8	113.7	117.4	116.1	110.0
253	224.7	114.2	117.9	116.6	110.5
254	225.6	114.7	118.4	117.1	111.0
255	226.5	115.2	118.9	117.6	111.5
256	227.4	115.7	119.4	118.1	112.0
257	228.3	116.1	119.9	118.6	112.5
258	229.2	116.6	120.4	119.1	113.0
259	230.1	117.1	120.9	119.6	113.5
260	231.0	117.6	121.4	120.1	114.0
261	231.8	118.1	121.9	120.6	114.5
262	232.7	118.6	122.4	121.1	115.0
263	233.6	119.0	122.9	121.6	115.5
264	234.5	119.5	123.4	122.1	116.0
265	235.4	120.0	123.9	122.6	116.5
266	236.3	120.5	124.4	123.1	117.0
267	237.2	121.0	124.9	123.6	117.5
268	238.1	121.5	125.4	124.1	118.0

TABLE IV—*Continued.*

Cuprous oxide (Cu_2O). Mgs.	Copper (Cu). Mgs.	*d*-Glucose. Mgs.	Invert sugar. Mgs.	Invert sugar and sucrose. 0.400 gram. Total mgs.	Invert sugar and sucrose. 2.0000 grams. Total mgs.
269	238.9	122.0	125.9	124.6	118.5
270	239.8	122.5	126.4	125.1	119.0
271	240.7	122.9	126.9	125.6	119.5
272	241.6	123.4	127.4	126.2	120.0
273	242.5	123.9	127.9	126.7	120.6
274	243.4	124.4	128.4	127.2	121.1
275	244.3	124.9	128.9	127.7	121.6
276	245.2	125.4	129.4	128.2	122.1
277	246.1	125.9	129.9	128.7	122.6
278	246.9	126.4	130.4	129.2	123.1
279	247.8	126.9	130.9	129.7	123.6
280	248.7	127.3	131.4	130.2	124.1
281	249.6	127.8	131.9	130.7	124.6
282	250.5	128.3	132.4	131.2	125.1
283	251.4	128.8	132.9	131.7	125.6
284	252.3	129.3	133.4	132.2	126.1
285	253.2	129.8	133.9	132.7	126.6
286	254.0	130.3	134.4	133.2	127.1
287	254.9	130.8	134.9	133.7	127.6
288	255.8	131.3	135.4	134.3	128.1
289	256.7	131.8	135.9	134.8	128.6
290	257.6	132.3	136.4	135.3	129.2
291	258.5	132.7	136.9	135.8	129.7
292	259.4	133.2	137.4	136.3	130.2
293	260.3	133.7	137.9	136.8	130.7
294	261.2	134.2	138.4	137.3	131.2
295	262.0	134.7	138.9	137.8	131.7
296	262.9	135.2	139.4	138.3	132.2
297	263.8	135.7	140.0	138.8	132.7
298	264.7	136.2	140.5	139.4	133.2
299	265.6	136.7	141.0	139.9	133.7
300	266.5	137.2	141.5	140.4	134.2
301	267.4	137.7	142.0	140.9	134.8
302	268.3	138.2	142.5	141.4	135.3
303	269.1	138.7	143.0	141.9	135.8
304	270.0	139.2	143.5	142.4	136.3
305	270.9	139.7	144.0	142.9	136.8

TABLE IV—*Continued.*

Cuprous oxide (Cu_2O). Mgs.	Copper (Cu). Mgs.	*d*-Glucose. Mgs.	Invert sugar. Mgs.	Invert sugar and sucrose. 0.400 gram. Total mgs.	Invert sugar and sucrose. 2.0000 grams. Total mgs.
306	271.8	140.2	144.5	143.4	137.3
307	272.7	140.7	145.0	144.0	137.8
308	273.6	141.2	145.5	144.5	138.3
309	274.5	141.7	146.1	145.0	138.8
310	275.4	142.2	146.6	145.5	139.4
311	276.3	142.7	147.1	146.0	139.9
312	277.1	143.2	147.6	146.5	140.4
313	278.0	143.7	148.1	147.0	140.9
314	278.9	144.2	148.6	147.6	141.4
315	279.8	144.7	149.1	148.1	141.9
316	280.7	145.2	149.6	148.6	142.4
317	281.6	145.7	150.1	149.1	143.0
318	282.5	146.2	150.7	149.6	143.5
319	283.4	146.7	151.2	150.1	144.0
320	284.2	147.2	151.7	150.7	144.5
321	285.1	147.7	152.2	151.2	145.0
322	286.0	148.2	152.7	151.7	145.5
323	286.9	148.7	153.2	152.2	146.0
324	287.8	149.2	153.7	152.7	146.6
325	288.7	149.7	154.3	153.2	147.1
326	289.6	150.2	154.8	153.8	147.6
327	290.5	150.7	155.3	154.3	148.1
328	291.4	151.2	155.8	154.8	148.6
329	292.2	151.7	156.3	155.3	149.1
330	293.1	152.2	156.8	155.8	149.7
331	294.0	152.7	157.3	156.4	150.2
332	294.9	153.2	157.9	156.9	150.7
333	295.8	153.7	158.4	157.4	151.2
334	296.7	154.2	158.9	157.9	151.7
335	297.6	154.7	159.4	158.4	152.3
336	298.5	155.2	159.9	159.0	152.8
337	299.3	155.8	160.5	159.5	153.3
338	300.2	156.3	161.0	160.0	153.8
339	301.1	156.8	161.5	160.5	154.3
340	302.0	157.3	162.0	161.0	154.8
341	302.9	157.8	162.5	161.6	155.4
342	303.8	158.3	163.1	162.1	155.9

TABLE IV—*Continued.*

Cuprous oxide (Cu_2O). Mgs.	Copper (Cu). Mgs.	*d*-Glucose. Mgs.	Invert sugar. Mgs.	Invert sugar and sucrose. 0.400 gram. Total Mgs.	Invert sugar and sucrose. 2.0000 grams. Total mgs.
343	304.7	158.8	163.6	162.6	156.4
344	305.6	159.3	164.1	163.1	156.9
345	306.5	159.8	164.6	163.7	157.5
346	307.3	160.3	165.1	164.2	158.0
347	308.2	160.8	165.7	164.7	158.5
348	309.1	161.4	166.2	165.2	159.0
349	310.0	161.9	166.7	165.7	159.5
350	310.9	162.4	167.2	166.3	160.1
351	311.8	162.9	167.7	166.8	160.6
352	312.7	163.4	168.3	167.3	161.1
353	313.6	163.9	168.8	167.8	101.6
354	314.4	164.4	169.3	168.4	162.2
355	315.3	164.9	169.8	168.9	162.7
356	316.2	165.4	170.4	169.4	163.2
357	317.1	166.0	170.9	170.0	163.7
358	318.0	166.5	171.4	170.5	164.3
359	318.9	167.0	171.9	171.0	164.8
360	319.8	167.5	172.5	171.5	165.3
361	320.7	168.0	173.0	172.1	165.8
362	321.6	168.5	173.5	172.6	166.4
363	322.4	169.0	174.0	173.1	166.9
364	323.3	169.6	174.6	173.7	167.4
365	324.2	170.1	175.1	174.2	167.9
366	325.1	170.6	175.6	174.7	168.5
367	326.0	171.1	176.1	175.2	169.0
368	326.9	171.6	176.7	175.8	169.5
369	327.8	172.1	177.2	176.3	170.0
370	328.7	172.7	177.7	176.8	170.6
371	329.5	173.2	178.3	177.4	171.1
372	330.4	173.7	178.8	177.9	171.6
373	331.3	174.2	179.3	178.4	172.2
374	332.2	174.7	179.8	179.0	172.7
375	333.1	175.3	180.4	179.5	173.2
376	334.0	175.8	180.9	180.0	173.7
377	334.9	176.3	181.4	180.6	174.3
378	335.8	176.8	182.0	181.1	174.8
379	336.7	177.3	182.5	181.6	175.3

TABLE IV—*Continued.*

Cuprous oxide (Cu_2O). Mgs.	Copper (Cu). Mgs.	*d*-Glucose. Mgs.	Invert sugar. Mgs.	Invert sugar and sucrose. 0.400 gram. Total mgs.	Invert sugar and sucrose. 2.0000 grams. Total mgs.
380	337.5	177.9	183.0	182.1	175.9
381	338.4	178.4	183.6	182.7	176.4
382	339.3	178.9	184.1	183.2	176.9
383	340.2	179.4	184.6	183.8	177.5
384	341.1	180.0	185.2	184.3	178.0
385	342.0	180.5	185.7	184.8	178.5
386	342.9	181.0	186.2	185.4	179.1
387	343.8	181.5	186.8	185.9	179.6
388	344.6	182.0	187.3	186.4	180.1
389	345.5	182.6	187.8	187.0	180.6
390	346.4	183.1	188.4	187.5	181.2
391	347.3	183.6	188.9	188.0	181.7
392	348.2	184.1	189.4	188.6	182.3
393	349.1	184.7	190.0	189.1	182.8
394	350.0	185.2	190.5	189.7	183.3
395	350.9	185.7	191.0	190.2	183.9
396	351.8	186.2	191.6	190.7	184.4
397	352.6	186.8	192.1	191.3	184.9
398	353.5	187.3	192.7	191.8	185.5
399	354.4	187.8	193.2	192.3	186.0
400	355.3	188.4	193.7	192.9	186.5
401	356.2	188.9	194.3	193.4	187.1
402	357.1	189.4	194.8	194.0	187.6
403	358.0	189.9	195.4	194.5	188.1
404	358.9	190.5	195.9	195.0	188.7
405	359.7	191.0	196.4	195.6	189.2
406	360.6	191.5	197.0	196.1	189.8
407	361.5	192.1	197.5	196.7	190.3
408	362.4	192.6	198.1	197.2	190.8
409	363.3	193.1	198.6	197.7	191.4
410	364.2	193.7	199.1	198.3	191.9
411	365.1	194.2	199.7	198.8	192.5
412	366.0	194.7	200.2	199.4	193.0
413	366.9	195.2	200.8	199.9	193.5
414	367.7	195.8	201.3	200.5	194.1
415	368.6	196.3	201.8	201.0	194.6
416	369.5	196.8	202.4	201.6	195.2

TABLE IV—*Continued.*

Cuprous oxide (Cu_2O). Mgs.	Copper (Cu). Mgs.	*d*-Glucose. Mgs.	Invert sugar. Mgs.	Invert sugar and sucrose. 0.400 gram. Total mgs.	Invert sugar and sucrose. 2.0000 grams. Total mgs.
417	370.4	197.4	202.9	202.1	195.7
418	371.3	197.9	203.5	202.6	196.2
419	372.2	198.4	204.0	203.2	196.8
420	373.1	199.0	204.6	203.7	197.3
421	374.0	199.5	205.1	204.3	197.9
422	374.8	200.1	205.7	204.8	198.4
423	375.7	200.6	206.2	205.4	198.9
424	376.6	201.1	206.7	205.9	199.5
425	377.5	201.7	207.3	206.5	200.0
426	378.4	202.2	207.8	207.0	200.6
427	379.3	202.8	208.4	207.6	201.1
428	380.2	203.3	208.9	208.1	201.7
429	381.1	203.8	209.5	208.7	202.2
430	382.0	204.4	210.0	209.2	202.7
431	382.8	204.9	210.6	209.8	203.3
432	383.7	205.5	211.1	210.3	203.8
433	384.6	206.0	211.7	210.9	204.4
434	385.5	206.5	212.2	211.4	204.9
435	386.4	207.1	212.8	212.0	205.5
436	387.3	207.6	213.3	212.5	206.0
437	388.2	208.2	213.9	213.1	206.6
438	389.1	208.7	214.4	213.6	207.1
439	390.0	209.2	215.0	214.2	207.7
440	390.8	209.8	215.5	214.7	208.2
441	391.7	210.3	216.1	215.3	208.8
442	392.6	210.9	216.6	215.8	209.3
443	393.5	211.4	217.2	216.4	209.9
444	394.4	212.0	217.8	216.9	210.4
445	395.3	212.5	218.3	217.5	211.0
446	396.2	213.1	218.9	218.0	211.5
447	397.1	213.6	219.4	218.6	212.1
448	397.9	214.1	220.0	219.1	212.6
449	398.8	214.7	220.5	219.7	213.2
450	399.7	215.2	221.1	220.2	213.7
451	400.6	215.8	221.6	220.8	214.3
452	401.5	216.3	222.2	221.4	214.8
453	402.4	216.9	222.8	221.9	215.4

TABLE IV—*Continued.*

Cuprous oxide (Cu_2O). Mgs.	Copper (Cu). Mgs.	*d*-Glucose. Mgs.	Invert sugar. Mgs.	Invert sugar and sucrose. 0.400 gram. Total mgs.	Invert sugar and sucrose. 2.0000 grams. Total mgs.
454	403.3	217.4	223.3	222.5	215.9
455	404.2	218.0	223.9	223.0	216.5
456	405.1	218.5	224.4	223.6	217.0
457	405.9	219.1	225.0	224.1	217.6
458	406.8	219.6	225.5	224.7	218.1
459	407.7	220.2	226.1	225.3	218.7
460	408.6	220.7	226.7	225.8	219.2
461	409.5	221.3	227.2	226.4	219.8
462	410.4	221.8	227.8	226.9	220.3
463	411.3	222.4	228.3	227.5	220.9
464	412.2	222.9	228.9	228.1	221.4
465	413.0	223.5	229.5	228.6	222.0
466	413.9	224.0	230.0	229.2	222.5
467	414.8	224.6	230.6	229.7	223.1
468	415.7	225.1	231.2	230.3	223.7
469	416.6	225.7	231.7	230.9	224.2
470	417.5	226.2	232.3	231.4	224.8
471	418.4	226.8	232.8	232.0	225.3
472	419.3	227.4	233.4	232.5	225.9
473	420.2	227.9	234.0	233.1	226.4
474	421.0	228.5	234.5	233.7	227.0
475	421.9	229.0	235.1	234.2	227.6
476	422.8	229.6	235.7	234.8	228.1
477	423.7	230.1	236.2	235.4	228.7
478	424.6	230.7	236.8	235.9	229.2
479	425.5	231.3	237.4	236.5	229.8
480	426.4	231.8	237.9	237.1	230.3
481	427.3	232.4	238.5	237.6	230.9
482	428.1	232.9	239.1	238.2	231.5
483	429.0	233.5	239.6	238.8	232.0
484	429.9	234.1	240.2	239.3	232.6
485	430.8	234.6	240.8	239.9	233.2
486	431.7	235.2	241.4	240.5	233.7
487	432.6	235.7	241.9	241.0	234.3
488	433.5	236.3	242.5	241.6	234.8
489	434.4	236.9	243.1	242.2	235.4
490	435.3	237.4	243.6	242.7	236.0

CONTRACTS LABORATORY.

A PROPOSED METHOD FOR EXAMINING BLEACHED FLOUR.

By Roscoe H. Shaw.

Received March 10, 1906.

The natural or "aging" process for bleaching flour is being rapidly superseded in western flouring mills by artificial methods. This fact has led to complaints from bakers who, having become accustomed to judge the quality of a flour to some extent by its color, are no longer able to distinguish the different grades as they previously did, since a poor grade may be bleached artificially to approach in whiteness a much higher grade.

Although there are several processes for artificial bleaching on the market, as far as the writer's knowledge goes the higher oxides of nitrogen play a part in each of them.

In searching for a chemical method for recognizing artificially bleached flour, the ground was taken that some nitro body might exist either as residual nitric oxide or as some nitro starch compound in flour so bleached that would not be present in natural flour, and if so its presence would serve as an identification.

The use of the well-known test for nitrates or certain other strong oxidizing agents, diphenylamine, was suggested by Dr. S. Avery of this university, who has used it successfully in detecting nitrates in organic matter.

In all, eight samples of flour were examined. Three of these were reported to have been bleached by the electric flaming discharge process, one by the electrochemical process, one by the straight chemical process, and one by the exothermic process. The other two were unbleached.

The method of procedure was as follows: About 1 kg. of flour was boiled for four hours with 95 per cent. alcohol in a balloon flask provided with a reflux condenser. After cooling, the liquid part was removed by filtering and the flour washed once with alcohol. The united extract and washings were evaporated nearly to dryness and this residue extracted with a mixture of equal parts of alcohol and ether. By allowing the first extract to cool before filtering, the most of the fat was removed and the alcohol-soluble proteids were not redissolved in the alcohol-ether extraction. The last extract was filtered and evaporated to a syrup in a 4-inch porcelain evaporating dish. The syrupy mass

was caused to spread itself in a film over the inside of the dish and a drop of a sulphuric acid solution of diphenylamine allowed to trail over the film.

The solution of diphenylamine was made by dissolving it in concentrated sulphuric acid and then diluting with water almost to the point of precipitation.

In each case where the flour was reported to have been artificially bleached the drop left a blue path, while no coloration was perceptible in the cases of the unbleached flour. In some instances the blue was not so sharp as might be wished for but was in all cases distinguishable.

A flour bleached by a process using ozone alone as a bleaching agent would probably not respond to the diphenylamine test. Such a process, however, is not used in the West to the writer's knowledge. It is also possible but highly improbable that a flour might be found which, fresh from the wheat, would yield the blue color when tested. To decide these points a much larger number of samples will be examined.

THE UNIVERSITY OF NEBRASKA,
LINCOLN, NEBRASKA.

[CONTRIBUTION FROM THE DIVISION OF FOODS, BUREAU OF CHEMISTRY, UNITED STATES DEPARTMENT OF AGRICULTURE.
SENT BY H. W. WILEY.]

GROWTH AND RIPENING OF PERSIMMONS.[1]

BY W. D. BIGELOW, H. C. GORE AND B. J. HOWARD.

Received April 3, 1906.

THE present work is a part of the systematic study of the ripening of fruits which we have undertaken, and regarding which two reports have already been made.[2] It has been found impossible to make as complete a study of the composition of a given fruit at various stages of its growth as is desirable, owing to the fact that some of the important constituents are present in many fruits in such a small amount that the limits of error of their estimation effectually preclude the possibility of determining the rate of their increase and decrease.

[1] Presented at the New Orleans Meeting of the American Chemical Society, December 30, 1905.

[2] U. S. Dept. Agr., Bur. Chem., Bull. 94, Studies on Apples, and U. S. Dept. Agri., Bur. Chem., Bull. 97, Studies on Peaches.

For this reason we have thought it advisable to select certain fruits because of their large percentage of constituents which in other fruits are present to a very small extent. It is not suggested that we can assume necessarily that a given constituent is subject to the same changes in all fruits. At the same time it is believed that the information gained by the study of the fruit in which a given constituent occurs in considerable quantity will be of value in affording a working hypothesis for the study of other fruits.

The persimmon was selected largely because of its content of a relatively large amount of tannin. This substance occurs in the apple and peach, regarding which studies have already been reported,[1] in such small amounts that the error of its determination is relatively large. Notwithstanding this, however, the tannin content is an important consideration with many fruits,[2] and its changes during the growth and ripening of the fruit are of considerable theoretical and practical importance.

The literature relating to the composition of persimmons is very meagre. The articles with which we are familiar are given in Table I. Besides the work on the fruit two articles[3] on persimmon products are included, and three articles[4] deal with the ripening of persimmons.

In the work here reported both wild (*Diospyros Virginiana L.*) and Japanese (*Diospyros Kaki L.*) persimmons were studied. Of the Japanese persimmons only the later stages of their ripening were considered. For the study of the growth of wild persimmons successive samples of fruit were taken from two trees during the growing season, and in addition examinations were made of fruit from a third tree at two periods of growth. The trees were located in Tacoma Park, Md. Tree No. 1 was located in the woods, tree No. 2 was located by a road-side, and tree No. 3 was on the edge of the woods. The fruit was gathered by one

[1] Loc. cit.

[2] E. g. in grapes to be used for wine-making, and in apples to be used for cider manufacture, see U. S. Dept. Agri., Bur. Chem., Bull. 71, p. 28.

[3] Ishii (Bull. Coll. Agri., Tokyo, **2**, 101 (1894)) obtained mannose from persimmon seed. Tsukamoto: Ibid. **4**, 329 (1900).

[4] Gerber: Annales des sciences naturelles, **4**, 1 (8) (1896). Also, Botanical Magazine, Tokyo, **14**, 179 (1900). Sawamura: Bull. Coll. Agric. Tokyo, **5**, 237 (1902).

of the writers on the morning of the day on which the analyses were made, care being taken at each picking to secure as representative a sample as possible by taking fruit from different sides of the tree, and from the upper and lower branches.

The sampling presents perhaps the greatest source of error in connection with a study of this nature. Since the results are to be calculated to the weight of each ingredient in a single fruit, they can only be correct when the average weight of the fruits of each sample is the same as the average weight of fruits on the tree at the time of picking. The difficulty of approximating the average sized fruit in making a sample is obvious. We have attempted to minimize this difficulty as far as possible by selecting a large number of fruits at each date of sampling.

The Japanese persimmons were secured through the Office of the Pomologist of the Department from the Experiment Station at Auburn, Alabama.

METHODS OF ANALYSIS.

The sample was weighed, calyx removed and weighed, and the pulp and seeds separated and weighed. In case of the wild, ripe persimmons the separation of the pulp and seeds was a matter of some difficulty as the seeds were enclosed by a slippery envelope, which must be cut (best with a dull knife edge) in order to separate the seed cleanly. In this study it was essential that the separation be sharply made. This was attained in all cases. The sample was passed through a food chopper, and received in a tightly closed sample jar from which the various portions were weighed out. The methods of the Association of Official Agricultural Chemists were followed in the main in the analysis of the pulp, but as some changes were introduced, the methods employed are given here in detail.

Determination of Total Solids.—Ten grams were weighed into a tared flat-bottomed lead dish, stirred to an even paste with a little water, and evaporated to nearly constant weight in a vacuum oven at a temperature not higher than 70°, and under a pressure of 100 to 200 mm.

Determination of Total Acid.—Ten grams were weighed in a counterpoised sugar dish, and washed into a beaker of about 400 cc. capacity with about 300 cc. of water, brought to a boil, cooled somewhat (while the beaker remained covered with a

watch-glass), titrated with tenth-normal sodium hydroxide, using phenolphthalein as indicator, and the result expressed as sulphuric acid.

Determination of Sugars.—The sugars were determined essentially as in our work with apples,[1] save that one-half normal solutions were employed, and any large excess of basic lead acetate was avoided.

Determination of Tannin.—Ten grams were weighed in a counterpoised sugar dish, transferred to a 200 cc. flask, and made up to the mark with water. After standing with frequent mixing for at least one hour, the mixture was filtered, and tannin determined in the filtrate by the Löwenthal-Proctor method as given by Allen.[2] The tannin was calculated as gallotannic acid.

Determination of Marc.—The term is used in this study to designate the material of the flesh of the persimmon which is insoluble in 95 per cent. alcohol. Water is generally employed in the estimations of marc, but in case of ripe persimmons, great difficulty is found in determining marc by water extraction methods because of the soft nature of the cell tissue, and its consequent tendency to pass through or to clog the pores of the filter. This difficulty is avoided by the use of alcohol instead of water. The details employed in the analysis of all samples follow.

Fifty grams of pulp were weighed in a counterpoised sugar dish, and washed into an Erlenmeyer flask with several volumes of strong alcohol (95 per cent.). It was then digested for several hours, or over night, on a steam-bath, at about the boiling-point of the alcohol, cooled, the material transferred to a mortar and thoroughly broken up with a pestle and thrown on a Büchner funnel, using a cloth filter and suction. The partially digested product was then returned to the flask, again digested with 95 per cent. alcohol, cooled, and again thrown on a filter as before, and this process repeated once or twice more. By this method all the sugar and other soluble matter, except mere traces, are removed. The marc is then transferred to a weighed aluminum dish, dried *in vacuo* at 70°, cooled and weighed. The temperature of 70° and vacuum drying were employed in order that in

[1] U. S. Dept. Agric., Bur. Chem., Bull. 94, p. 66.

[2] "Commercial Organic Analysis," Vol. III, Part 1, p. 74.

our analysis, the total determined matter without any correction could be added together for comparison with total solids.

The analyses of the persimmons are shown in Table II. The samples marked "Stored" were held in heavy card board boxes (mailing boxes) for the time indicated.

GROWTH AND RIPENING OF WILD PERSIMMONS.

In case of the fruit of trees No. 1 and No. 2, the trees from which five pickings of fruit were received, it will be noticed that the ratio of pulp to seeds gradually increases. The proportion of calyx rapidly falls from about 4 per cent. to about 1.5 per cent. of the weight of the fruit. The fruit from tree No. 3, of which only two pickings were obtained, was about twice as large as the fruit of tree No. 1 and nearly three times as large as that of tree No. 2. The first-mentioned also possessed a considerably larger proportion of pulp than that of the other two trees.

Review of Literature.—Practically no chemical work has been done on the study of the chemical changes that take place during the ripening of persimmons, although several writers have advanced theories regarding them. The theories of Gerber[1] have practically no chemical foundation, and merit the term "speculations" rather than "theories." Concerning the tannin change in the varieties of persimmons studied by him (*D. Kaki Zendi, D. Costata and D. Kaki Ochirakaki*), the author considers that the tannin does not give rise to sugars, but disappears by complete oxidation, forming carbon dioxide and water. Aso[2] considers it most probable that the tannin is gradually changed, perhaps by oxidation brought about by an oxidizing enzyme, and note that it accumulates in special cells. Oxidase was reported by Aso in the unripe fruit, and peroxidase and catalase in the ripe fruit.

Sawamura[3] gives three methods of curing persimmons, *viz.*: (1) keeping fruits for twelve hours in a barrel containing vapors of alcohol (generally freshly emptied sake barrels are used); (2) keeping fruits for twelve hours in warm water (30° to 40°); and (3) drying the peeled fruits in the sun. The tannin is believed by him to be changed to a tasteless substance by partial oxidation brought about by the enzymes in the fruit.

[1] Annales des sciences naturelles, 4, (8), 203.

[2] Botanical Magazine, Tokyo, 14, 179 (1900).

[3] Bull. Coll. Agric., Tokyo (1902).

By calculating to grams per persimmon the data given in Table II, we secure data regarding the actual gain and loss of the various ingredients in persimmons during the various stages of their life history.

In Fig. 1 is given the composition of wild persimmons grown on the tree in the woods, which we have designated as tree No. 1. This table is calculated on grams per fruit. It is especially noticeable that the weight of the pulp is less in the sample picked September 6th than in that picked a month previous. The total weights of solids and tannin are also lower in the sample picked September 6th, and the weight of sugar but slightly greater than in the sample picked on August 7th. The percentage of marc was not determined on September 2nd.

With the single exception of the sample noted, the weight of the pulp steadily increased until November 4th. A marked increase is also noted in the case of total determined solids, sugar and marc. In all the constituents above mentioned, the increase in weight was considerably more rapid between September 21st and October 13th than between October 13th and November 4th. The increase in the amount of marc, however, was greater in the first period mentioned than in the last. The weight of tannin increased very gradually from August 7th, the date of the first sample taken, to October 13th. From August 14th until November 4th the weight of tannin decreased somewhat rapidly, and the fact is somewhat striking and suggestive that tannin decreases during the period mentioned in proportion to the increase of marc. This will be discussed in greater detail later.

The changes in composition noted in tree No. 1 (Fig. 1) are identical with those in the fruit from tree No. 2 (Fig. 2) with the exception of the probable error previously noted in the size of the fruits in the sample taken from tree No. 1 on September 6th, and with the further exception that in the fruit from tree No. 2 the weight of the pulp, determined solids, and reducing sugar decreased, and the weight of total solids increased but slightly after October 13th. It appears that the fruit from tree No. 2 was in a more mature state on October 13th than the fruit from tree No. 1. It separated much more readily from the tree, and the loss in the weight of soluble solids and reducing sugar in the fruit from tree No. 2 after October 13th indicates that the fruit had reached its full maturity on the date mentioned. It is to be

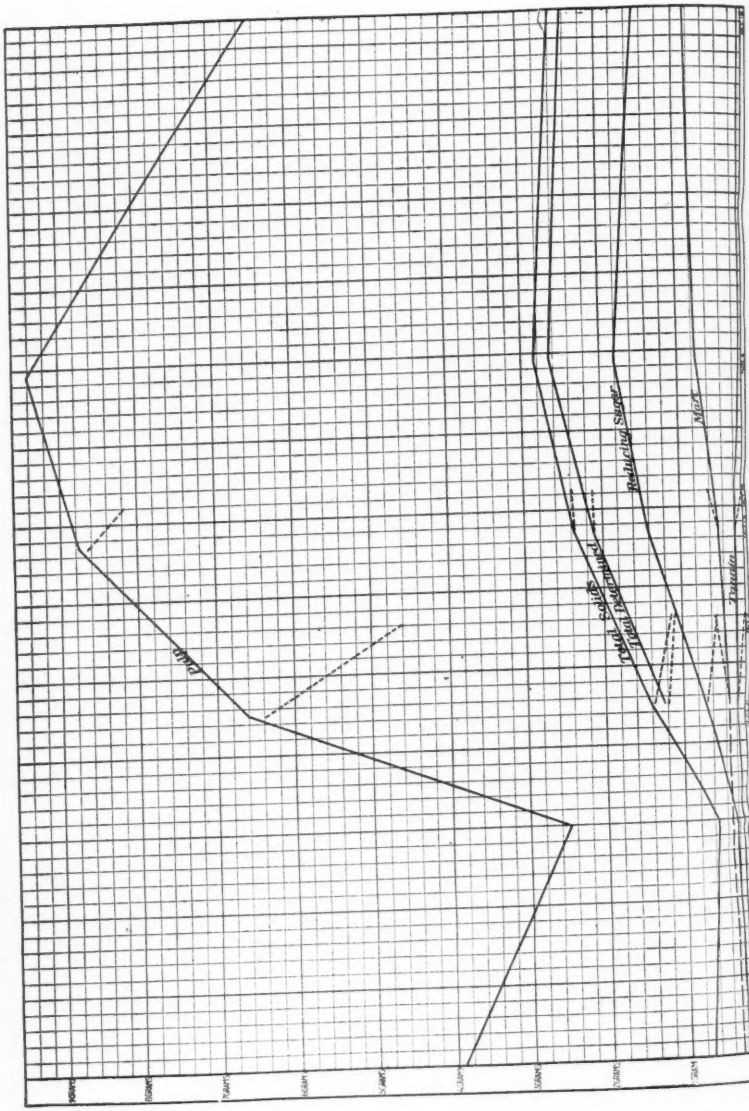

Total Solids
Total Undetermined
Reducing Sugar
Ash
Protein

TABLE I.—ANALYSES OF PERSIMMONS.

Composition of persimmon pulp expressed as per cent. of pulp.

Date.	Variety.	Author.	Weight per persimmon. Grams.	Pulp. Per cent.	Seeds. Per cent.	Solids. Per cent.	Reducing sugar. Per cent.	Acid. Per cent.	Ether extract.
1888	*Diospyros Virginiana*	Parsons[1]	.....	.....	.....	33.88	13.54[7]	none	0.
1895	*Diospyros Kaki Hiyakume*	Colby[2]	175.0	.....	.....	.....	18.20	.....	.
1896	*Diospyros Virginiana*, Sample No. 1[8]	Huston-Barrett[3]	14.1	86.15	13.85	29.10	.....	.....	0.
1896	*Diospyros Virginiana*, Sample No. 5	Huston-Barrett	19.3	82.58	17.42	28.92	.....	.....	0.
1896	*Diospyros Virginiana*, Sample No. 6	Huston-Barrett	14.1	83.33	16.67	35.70	.....	.....	0.
1896	*Diospyros Virginiana*, Sample No. 7	Huston-Barrett	6.3	85.24	14.76	34.99	.....	.....	0.
1896	*Diospyros Virginiana*, Sample No. 8	Huston-Barrett	5.9	82.00	18.00	48.21	.....	.....	0.
1896	*Diospyros Virginiana*, Sample No. 9[9]	Huston-Barrett	14.0	88.50	11.50	38.14	.....	.....	0.
1898	*Diospyros Kaki Hachiya*	McBryde[4]	180	seedless		28.23	.....	0.13[10]	ca
1898	*Diospyros Kaki Tsuru*	McBryde	194	seedless		26.54	.....	0.16	
1898	*Diospyros Kaki Hiyakume*	McBryde	175	.....	1.71	29.83	.....	0.13	
1898	*Diospyros Kaki Yemon*	McBryde	150	seedless		23.74	.....	0.10	
1898	*Diospyros Kaki* Japanese graft on native	McBryde	103	seedless		25.00	.....	0.11	
1898	*Diospyros Virginiana*	McBryde	6.6	.....	15.5	33.22	.....	0.26	
1898	*Diospyros Virginiana*	McBryde	8.9	.....	17.5	42.76	.....	0.15	
1898	*Diospyros Virginiana*	McBryde	9.2	.....	16.3	42.75	.....	0.17	
1902	*Diospyros Kaki*, large seedling	Jaffa[5]	.....	.....	22.4[11]	22.96	19.39	.....	0.
1902	*Diospyros Kaki Tane nashi*	Jaffa	.....	.....	18.8	18.07	12.81	.....	0.
1902	*Diospyros Kaki Yemon*	Jaffa	.....	.....	30.7	18.34	13.19	.....	0.

Composition of persimmon pulp expressed as per cent. of total fruit.

Diospyros Kaki, sweet variety	Jaffa[6]	.....	.....	3.29[12]	17.97	.....	.....	0.
Diospyros Kaki, astringent variety	Jaffa	.....	.....	2.76	16.35	.....	.....	0.

[1] Am. Ch. J. 10, 488 (1888).

[2] Cal. Sta. Rept., 1895, p. 183.

[3] Indiana Expt. Sta., 1896, Bull. 60, p. 51.

[4] Tenn. Sta. 11, 220 (1898).

[5] U. S. Dept. Agric. O. E. S. Bull. 132, p. 9.

[6] Tokyo Sanitary Expt. Sta. through Samamura Bull. Coll. of Agric., Tokyo, 5, 237 (1902).

[7] Sucrose also reported 1.03 per cent.

[8] Of this sample, the ash of the pulp and of the seed was analyzed, the analysis of seed given and the pulp are reported.

Analysis of ash.	SiO_2. Per cent.	Fe_2O_3. Per cent.	Mn_3O_4. Per cent.	CaO. Per cent.	MgO. Per cent.	P_2O_5. Per cent.	SO_3. Per cent.	K_2O. Per cent.	Na_2O. Per cent.	CO_2. Per cent
Pulp	1.52	0.44	0.06	4.74	2.23	7 26	6.84	53.45	2.36	15.94
Seed	20.12	1.19	0.10	6.76	6.96	13.36	10.53	37.62	0.82	0.00

Analysis of seed.	Solids.	Ether extract.	Crude fiber.	Ash.	Nitrogen-free extract.	Nitrogenous matter.	Albumoids.
	90.14	3.04	17.60	2.07	56 83	10.60	8.10

Results of special methods applied to air-dry pulp (containing 3.84 per cent. H_2O):

Treated successively with:	Per cent. dissolve
Chloroform	2.76
80 per cent. alcohol	47.22
Cold water	14.10
Boiling water, 2 hours	4.99
Boiling 1¼ per cent. H_2SO_4, 1 hour	6.26
Boiling 1¼ per cent. NaOH, 1 hour	18.61

[9] Cultivated.

[10] Presumably calculated as malic.

[11] Refuse.

[12] Fiber and seeds.

TABLE I.—ANALYSES OF PERSIMMONS.

ion of persimmon pulp expressed as per cent. of pulp.

Author.	Weight per persimmon. Grams.	Pulp. Per cent.	Seeds. Per cent.	Solids. Per cent.	Reducing sugar. Per cent.	Acid. Per cent.	Ether extract. Per cent.	Nitrogen-free extract. Per cent.	Crude fiber. Per cent.	Ash. Per cent.	Nitrogenous
rsons[1]	.....	.....	.....	33.88	13.54[7]	none	0.70	29.71	1.78	0.86	c
lby[2]	175.0	.....	.....	.....	18.20	.....	.....	.....	.....	.....	
ston-Barrett[3]	14.1	86.15	13.85	29.10	.....	.....	0.42	25.54	1.30	0.63	1
ston-Barrett	19.3	82.58	17.42	28.92	.....	.....	0.23	26.30	1.02	0.75	c
ston-Barrett	14.1	83.33	16.67	35.70	.....	.....	0.33	32.18	1.56	0.70	c
ston-Barrett	6.3	85.24	14.76	34.99	.....	.....	0.36	31.34	1.60	0.83	c
ston-Barrett	5.9	82.00	18.00	48.21	.....	.....	0.42	43.88	1.83	1.04	1
ston-Barrett	14.0	88.50	11.50	38.14	.....	.....	0.16	31.33	1.26	0.73	c
							Fats and carbohydrates.				
cBryde[4]	180		seedless	28.23	.....	0.13[10]		26.42	.....	0.88	c
cBryde	194		seedless	26.54	.....	0.16		25.16	.....	0.64	c
cBryde	175	.....	1.71	29.83	.....	0.13		27.58	.....	1.15	1
cBryde	150		seedless	23.74	.....	0.10		22.69	.....	0.60	c
cBryde	103		seedless	25.00	.....	0.11		24.13	.....	0.45	c
cBryde	6.6	.....	15.5	33.22	.....	0.26		31.32	.....	1.26	c
cBryde	8.9	.....	17.5	42.76	.....	0.15		41.34	.....	0.84	c
cBryde	9.2	.....	16.3	42.75	.....	0.17		40.99	.....	1.28	c
ffa[5]	.....	.....	22.4[11]	22.96	19.39	.....	0.31	.....	0.93	0.72	1
ffa	.....	.....	18.8	18.07	12.81	.....	0.55	.....	2.93	0.62	1
ffa	.....	.....	30.7	18.34	13.19	.....	0.85	.....	2.37	0.61	1
of persimmon pulp expressed as per cent. of total fruit.											
ffa[6]	.....	.....	3.29[12]	17.97	.....	.....	0.03	13.62	.....	0.43	0
ffa	.....	.....	2.76	16.35	.....	.....	0.02	12.56	.....	0.43	0

ra Bull. Coll. of Agric., Tokyo, 5, 237 (1902).

the seed was analyzed, the analysis of seed given and the results of special methods

CaO. Per cent.	MgO. Per cent.	P_2O_5. Per cent.	SO_3. Per cent.	K_2O. Per cent.	Na_2O. Per cent.	CO_2. Per cent.	Cl. Per cent.	H_2O. Per cent.	Total Per cent
4.74	2.23	7 26	6.84	53.45	2.36	15.94	0.30	4.32	99.46
6.76	6.96	13.36	10.53	37.62	0.82	0.00	0.11	2.52	100.09

Ash.	Nitrogen-free extract.	Nitrogenous matter.	Albumoids.
2.07	56 83	10.60	8.10

r-dry pulp (containing 3.84 per cent. H_2O):

ively with:

	Per cent. dissolved.
rm	2.76
nt. alcohol	47.22
er	14.10
vater, 2 hours	4.99
¼ per cent. H_2SO_4, 1 hour	6.26
¼ per cent. NaOH, 1 hour	18.61

Per cent.	Ash. Per cent.	Nitrogenous matter. Per cent.	Albuminoids. Per cent.	Heat of combustion per gram. Calories.
.78	0.86	0.83	.....	.....
....	.....	.....	.....	.....
.30	0.63	1.21	0.98	.....
.02	0.75	0.62	0.53	.....
.56	0.70	0.93	0.78	.....
.60	0.83	0.86	0.81	.....
.83	1.04	1.04	0.94	.....
.26	0.73	0.66	0.48	.....
....	0.88	0.93	.....	.....
....	0.64	0.74	.....	.....
....	1.15	1.10	.....	.....
....	0.60	0.45	.....	.....
....	0.45	0.42	.....	.....
...	1.26	0.64	.....	.....
...	0.84	0.58	.....	.....
...	1.28	0.48	.....	.....
93	0.72	1.61	.....	0.429
93	0.62	1.16	.....	0.346
37	0.61	1.32	.....	0.376
...	0.43	0.61	.....	.....
...	0.43	0.58	.....	.....

cial methods applied to the

H_2O. r cent.	Total. Per cent.
.32	99.46
.52	100.09

TABLE II.—COMPOSITION OF PERSIMMONS

Serial number.	Variety.	Date.	Composition of whole fruit. Weight per fruit. Grams.	Pulp. Per cent.	Seeds. Per cent.	Calyx. Per cent.
14474	Wild persimmon, Tree No. 1	Aug. 7, 1905	4.97	75.4	21.1	3.5
15176	Wild persimmon, Tree No. 1	Sept. 6, 1905	3.43	72.3	25.7	2.0
15301	Wild persimmon, Tree No. 1	Sept. 21, 1905	8.58	76.5	21.9	1.6
15318	Wild persimmon, Tree No. 1, stored 11 days	Oct. 2, 1905	6.48	71.4	27.4	1.2
15334	Wild persimmon, Tree No. 1	Oct. 13, 1905	11.15	77.8	21.0	1.2
15348	Wild persimmon, Tree No. 1, stored 5 days	Oct. 18, 1905	10.37	78.8	20.0	1.2
15434	Wild persimmon, Tree No. 1	Nov. 4, 1905	11.75	79.9	18.5	1.6
15532	Wild persimmon, Tree No. 1	Dec. 18, 1905	8.68	75.0	22.9	2.1
14475	Wild persimmon, Tree No. 2	Aug. 7, 1905	4.58	62.1	33.1	4.8
15177	Wild persimmon, Tree No. 2	Sept. 6, 1905	5.90	69.8	27.9	2.3
15302	Wild persimmon, Tree No. 2	Sept. 21, 1905	7.32	76.9	21.3	1.8
15317	Wild persimmon, Tree No. 2, stored 9 days	Sept. 30, 1905	6.40	75.1	23.4	1.5
15335	Wild persimmon, Tree No. 2	Sept. 13, 1905	7.94	78.4	20.4	1.2
15349	Wild persimmon, Tree No. 2, stored 5 days	Sept. 18, 1905	7.18	79.5	19.5	1.0
15440	Wild persimmon, Tree No. 2	Nov. 7, 1905	6.63	79.5	18.9	1.5
15327	Wild persimmon, Tree No. 3	Oct. 4, 1905	20.51	89.3	9.0	1.7
15332	Wild persimmon, Tree No. 3, stored 8 days	Oct. 12, 1905	17.21	87.6	11.0	1.4
15375	Wild persimmon, Tree No. 3	Oct. 23, 1905	19.61	87.9[1]	10.8[1]	1.3[1]
15405	Wild persimmon, Tree No. 3, stored 7 days	Oct. 30, 1905	18.00	87.9	10.8	1.3
15391	Japanese persimmons,[2] "Hachiya"	Oct. 26, 1905	137.7	97.6	1.0	1.4
15445	Japanese persimmons, stored 25 days	Nov. 20, 1905	114.6	97.7	0.9	1.4
15392	Japanese persimmons,[2] "Tsurunoko"	Oct. 26, 1905	86.15	96.0	2.9	1.1
15442	Japanese persimmons, stored 14 days	Nov. 9, 1905	75.00	96.0	2.5	1.5
15179	Persimmon must from unripe wild persimmons	Sept. 8, 1905	sp. gr. 1.0805	.....	...	...

[1] Error, used proportion of pulp, seed and calyx found in stored fruit.

[2] Quotation marks indicate that these fruits were from scions imported under the variet

—COMPOSITION OF PERSIMMONS AT DIFFERENT PERIODS OF GROW

Date.	Composition of whole fruit. Weight per fruit. Grams.	Pulp. Per cent.	Seeds. Per cent.	Calyx. Per cent.	Solids. Per cent.	Marc. Per cent.	Acid as H_2SO_4. Per cent.	Reducing sugar invert. Per cent.	Polar Direct.
g. 7, 1905	4.97	75.4	21.1	3.5	18.38	6.81	.....	4.45.	—0.9
t. 6, 1905	3.43	72.3	25.7	2.0	21.39	.....	0.49	8.51	—2.35
t. 21, 1905	8.58	76.5	21.9	1.6	21.43	5.24	0.27	10.78	—3.6
. 2, 1905	6.48	71.4	27.4	1.2	24.91	12.03	0.29	11.45	...
. 13, 1905	11.15	77.8	21.0	1.2	27.26	5.45	0.36	16.31	...
. 18, 1905	10.37	78.8	20.0	1.2	29.32	7.74	0.33	17.72	—4.6
. 4, 1905	11.75	79.9	18.5	1.6	30.24	7.88	0.37	19.29	—5.4
. 18, 1905	8.68	75.0	22.9	2.1	40.12	13.20	0.39	23.42	—7.2
g. 7, 1905	4.58	62.1	33.1	4.8	22.41	8.28	.....	5.30	—1.0
t. 6, 1905	5.90	69.8	27.9	2.3	25.13	.....	0.44	9.77	—2.4
t. 21, 1905	7.32	76.9	21.3	1.8	24.66	5.86	0.26	13.16	—4.0
t. 30, 1905	6.40	75.1	23.4	1.5	28.82	12.59	0.12	13.84	...
t. 13, 1905	7.94	78.4	20.4	1.2	29.61	6.48	0.27	18.05	...
t. 18, 1905	7.18	79.5	19.5	1.0	32.56	10.42	0.24	19.18	—5.0
. 7, 1905	6.63	79.5	18.9	1.5	35.86	9.14	0.22	21.02	—5.8
4, 1905	20.51	89.3	9.0	1.7	23.62	4.38	0.24	14.67	—4.6
12, 1905	17.21	87.6	11.0	1.4	27.54	8.09	0.23	16.84	...
23, 1905	19.61	87.9[1]	10.8[1]	1.3[1]	27.16	6.86	0.36	17.09	—4.5
30, 1905	18.00	87.9	10.8	1.3	28.77	6.67	0.40	17.91	...
26, 1905	137.7	97.6	1.0	1.4	20.75	4.40	0.11	14.57	—3.9
20, 1905	114.6	97.7	0.9	1.4	23.61	5.70	0.14	17.28	—2.8
26, 1905	86.15	96.0	2.9	1.1	22.71	3.52	0.10	17.26	—4.3
9, 1905	75.00	96.0	2.5	1.5	25.38	5.09	0.06	19.44	—3.8
8, 1905	sp. gr. 1.0805	...	...	...	21.05	.....	0.51	9.95	—2.4

l in stored fruit.

scions imported under the variety named, and grafted on American s

Analysis of pulp.									
Sugar invert. Per cent.	Polarizations. Direct.	Invert.	Soluble tannin. Per cent.	Total nitrogen. Per cent.	Soluble nitrogen. Per cent.	Ash. Per cent.	Determined solids.	Undetermined solids.
.45	—0.9	—1.1 @28°	2.60	.....	.....	.....	.....	.....
.51	—2.35	—2.5 @27°	3.38	.....	.....	.....	.....	.....
.78	—3.6	—3.9 @25°	2.50	.....	.....	.....	18.79	2.64
.45	...	.....	traces	.....	.....	.....	23.77	1.14
.31	...	.....	2.14	0.173	0.087	0.77	24.26	3.00
.72	—4.6	—4.6 @24°	traces	0.177	0.098	.....	25.79	3.53
.29	—5.4	—6.0 @21°	0.54	.....	.....	.....	28.08	2.16
.42	—7.2	—7.4 @24°	0.82	.....	.....	.....	37.83	2.29
.30	—1.0	—0.9 @28°	3.91	.....	.....	.....	.....	.....
.77	—2.4	—2.75@27°	3.98	.....	.....	.....	.....	.....
.16	—4.0	—4.4 @25°	3.00	.....	.....	.....	22.28	2.38
.84	...	.....	traces	.....	.....	.....	26.55	2.27
.05	...	.....	1.98	0.135	0.074	0.65	26.78	2.83
.18	—5.0	—5.0 @24°	traces	0.155	0.079	.....	29.84	2.72
.02	—5.8	—6.2 @24°	traces	.....	.....	.....	30.38	5.48
67	—4.6	—4.18@24°	2.47	0.074	0.028	0.62	21.76	1.86
.84	...	.....	traces	0.100	0.051	.....	25.16	2.38
09	—4.5	—4.6 @21°	2.01	0.126	0.052	0.82	26.32	0.84
91	...	—4.84@22°	1.14	.....	.....	.....	26.12	2.65
57	—3.9	—3.7 @20°	0.68	0.100	0.045	.....	19.76	0.99
.28	—2.8	—3.08@22°	traces	.....	.... .	.....	23.12	0.49
26	—4.3	—4.6 @20°	0.34	0.086	0.027	.....	21.22	1.49
44	—3.8	—4.0 @24°	traces	.....	.....	.....	24.59	0.79
95	—2.4	—3.6 @27°	6.17	.....	.....	.....	16.63	4.42

American stock, but were not true to name.

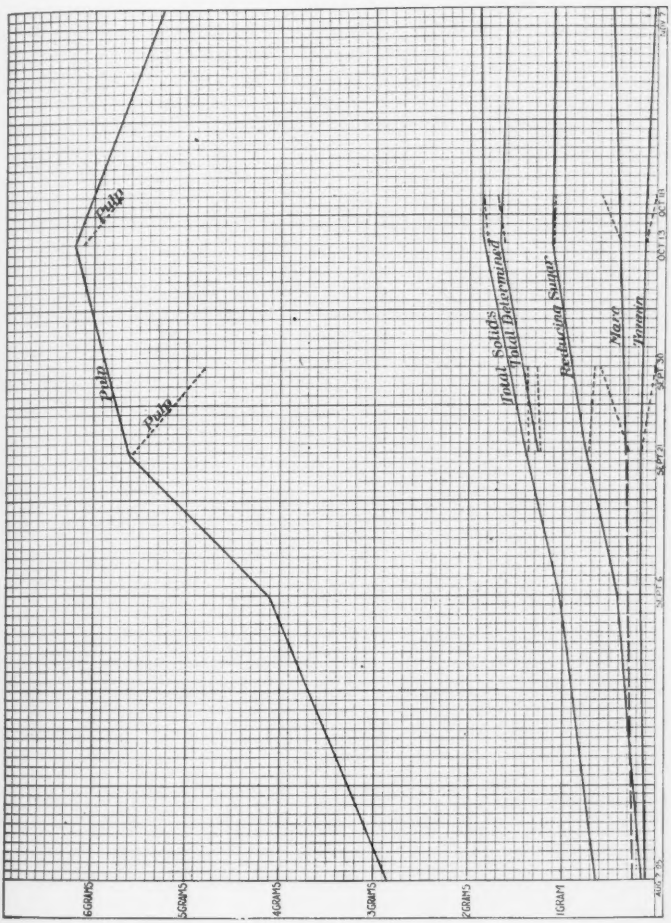


Fig. 2.—Chart showing chemical changes during growth and storage of wild persimmons (*D. Virginiana*) from tree No. 2, in grams per persimmon. Stored samples.

expected that after full maturity was attained a loss in reducing sugars and soluble solids would occur as this was found to be the case in apples and peaches.[1] In Fig. 2 as in Fig. 1, we note a corresponding increase in marc and decrease in tannin.

The results from the examination of the fruit of tree No. 3

[1] Loc. cit., see p. 689.

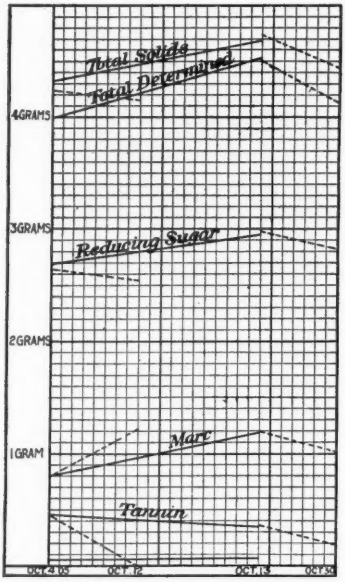


Fig. 3.—Chart showing chemical changes during growth and storage of wild persimmons (*D. Virginiana*) from tree No. 3, in grams per persimmon. Stored samples.

are given on the basis of grams per fruit in Fig. 3. As stated above the study of this fruit was begun late in the season, but the results are of interest as they confirm the results obtained from the fruit of the other two trees.

DISCUSSION OF RESULTS ON STORAGE.

As noted before (see p. 692) sub-samples of wild persimmons were stored in mailing boxes at laboratory temperature, at several times of picking. In all cases, a very marked acceleration of ripening took place. Such acceleration of ripening due to picking is a matter of common experience with fruits.[1] The weight and number of the fruits before storage were noted. As soon as the fruit had undergone the characteristic softening accompanied by the disappearance or marked lessening of the tannin the sample was again weighed and analyzed. The results are shown in Table II, and are plotted in Figs. 1, 2 and 3 in dotted

[1] See e. g. the acceleration of the ripening noted in case of unripe apples. U. S. Dept. Agric., Bur. Chem., Bull. 94, p. 51.

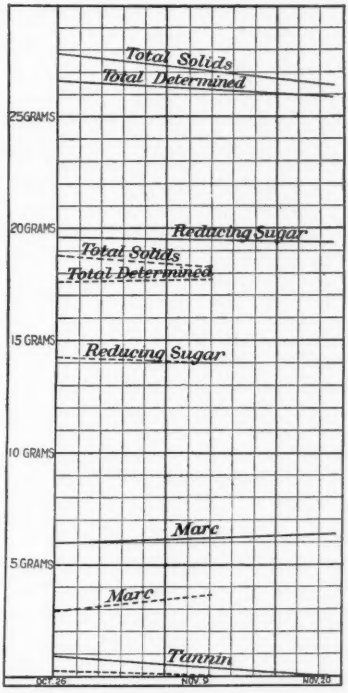


Fig. 4.—Chart showing the chemical changes during storage of two varieties of Japanese persimmons, in grams per persimmon. "Hachiga," "Tsurunoko."

lines on the basis of grams of constituent per fruit. During the storage marked desiccation took place. This accounts largely for the loss in the weight of the pulp.

Six experiments of this kind were carried on in the case of wild persimmons, and two experiments in case of Japanese persimmons (see Fig. 4). While the wild persimmons, in four cases out of six, the analyses showed a distinct loss of total solids, in two cases a slight gain of total solids appeared. The determined solids practically paralleled the total solids in five cases out of six. In one case, however (Fig. 2, analyses of September 21st and October 2nd), the two lines converge. The reducing sugars decreased in five cases out of six. This loss is probably due to consumption of sugars in respiration. To this loss in sugar is probably due the loss in total solids and in determined solids.

The marc increases sharply in five cases out of six, while the tannin decreases notably in all cases. Very similar results were obtained with Japanese persimmons (see Fig. 4), save that the changes were much slower. In Fig. 3, analyses on October 23rd and October 30th, the usual increase of marc was not observed. The tannin, however, did not fall to its usual minimum. The complete change of the tannin had not ensued, and it is possible that the tannin which was incompletely converted into the insoluble form, was partially soluble in the alcohol employed in the method for marc. The results on the marc would therefore be too low. This view is in part supported by the fact that the amount of determined solids has decreased somewhat faster than the loss in total solids or total sugar.

The chemical changes during ripening in storage are therefore as follows. There is a distinct loss in total solids, determined solids, and sugar. There is a notable increase in marc (in several cases the marc is more than doubled) and a corresponding decrease in tannin.

In comparison with the changes which take place in the normal growth of the persimmon, those which take place on storage of the picked fruit at room temperature are very different in some particulars, and very similar in others. While in the normally growing fruit an increase in solids and sugar is noted, decreases are found in the solids and sugar of stored fruit. This is not different from the usual experience with stored fruits.[1] The changes in marc and tannin, however, are very similar in the stored fruit to those which take place in the growing fruit.

The tannin of unripe persimmons possesses very peculiar properties. Some of these are described by Tsukamoto.[2] The product Kaki-shibu is made from a small astringent variety of Japanese persimmon by crushing in water and allowing the product to ferment. Owing to the property of the tannin of forming insoluble films on drying, the product is applied to fish lines, to packing paper for tea, and to various other articles. The tannin of the fermented product was found by Tsukamoto to give no precipitate with alcohol, but is precipitated by a

[1] See e. g. in case of apples, U. S. Dept. Agri., Bur. Chem., Bull. 94, pp. 57–58.

[2] On Kaki-shibu, a fruit juice in technical application in Japan. Bull. Coll. Agric. Tokyo, 4, 329 (1900–1902).

mixture of alcohol and ether. It is also precipitated by strong mineral acids and by acetic acid. We have not extended the observations of this writer, but have confirmed them. The insoluble tannin in the marc readily becomes soluble on warming with dilute mineral acid.

GENERAL DISCUSSION.

The normal ripening may be considered to begin about September 21st, in the case of the fruit on trees No. 1 and 2, the color change from green to golden yellow having taken place just before this date. Ripening had already started in the fruit of tree No. 3 on October 4th, the time of the first examination.

The two features in connection with the data presented herewith regarding the ripening of fruit which occur to us as most noteworthy, and perhaps least expected, are first the increase in the actual weight of sugar, total solids, and determined solids in each fruit after the growing season was supposed to be over, and second, the relation between the marc and the tannin. The first killing frosts in the locality where these persimmons were grown occurred on October 22nd, and freezing temperatures are recorded on four dates between October 13th and November 7th. On November 3rd a temperature of 30° is recorded. Notwithstanding this fact, it appears that the circulation in the persimmon tree during the period mentioned continued.

Duplicates on our determinations were steadily concordant. The ratios of sugar to determined solids, and of determined solids to total solids are uniformly consistent, and we see no reason to doubt the correctness of the results here presented. The only possibility of their incorrectness is a possible error in sampling, such as we have suggested probably occurred in the case of the sample from tree No. 1, taken September 6th. When we consider, however, that samples were taken from three trees, and that the results are all consistent with each other, we are forced to the conclusion that an actual increase in the weight of sugar and soluble solids occurred after freezing weather had begun. In the case of the fruit from tree No. 1 (Fig. 1) this increase continued up to the time of the sampling on November 4th. In the fruit from tree No. 2, however, there was no further increase after October 13th.

We find nothing in our results to explain the formation of sugar. The absence of sucrose and the occurrence of all of the

sugar in the form of reducing sugar is interesting. The percentage of acid is very small in the persimmon, and there was no apparent increase or decrease during the life history of the fruit. This last may be partly due to the small amount of acid, and the consequent relatively large error in its determination.

It is an interesting fact that on October 18th the fruit on tree No. 1 clung to the tree tenaciously, and the stems were apparently alive, whereas the fruit of tree No. 2 which had probably attained full maturity was readily separated from the tree. Another fact that is of striking interest is that the sum of marc and soluble tannin was almost uniform during the entire period of our observation of the fruit.

Both marc and tannin increased in weight very slightly from August 7th to September 21st. After September 21st in the fruit from the three trees of wild persimmons which have already been discussed, and in the two varieties of Japanese persimmons, the weight of marc increased while the weight of tannin showed a corresponding decrease.

We had intended the pickings of November 4th and 7th should be the last. Since the weight of sugar and other solids appeared to be increasing at that time, however, it seemed desirable to secure still another sample, if possible, for comparison with those previously examined. The fruit was still clinging to tree No. 1, though it had all fallen from tree No. 2. Accordingly a large sample (70 fruits) was secured on December 18th from tree No. 1. The results of the analysis show considerable desiccation, but no marked changes in the constituents. During the interval between November 4th and December 18th, temperatures below freezing were recorded twenty-eight times, and on December 1st a temperature of 13° F. was recorded.

The following theories to account for the disappearance of tannin seem worthy of consideration:

First, that it is decomposed with the formation of carbon dioxide and water, owing to the respiration of the fruit.

Second, that it is converted into sugar.

Third, that it is converted into undetermined solids.

Fourth, that it unites with some constituent of the undetermined solids.

Fifth, that it unites with the marc with the formation of an insoluble compound.

Sixth, that it is converted into an insoluble form.

The first theory was advanced by Gerber (see p. 692) as a result of investigations which appear to be very inadequate. We have satisfactorily demonstrated in our studies of the ripening of other fruits that the respiration of those fruits is accounted for by the diminution of sugar,[1] whereas their content of tannin was not sufficient to furnish the amount of carbon dioxide liberated during the respiration of the fruit. Here, again, we find the sugars decrease materially on storage of the fruit, and the loss of sugar sustained is evidently sufficient to account for the respiration during storage.

We are not aware that the second theory mentioned has been advanced as the result of any experimental work. It is the general impression, however, and was the impression of the writers when this study was begun, that the tannin was probably converted into sugar as the fruit ripened. If this were true, however, we should not look for the parallelism that exists between the total solids and sugar, but rather we would expect that the total solids should increase less rapidly than the sugars.

The same argument may be advanced with reference to the third theory. This possibility seems to be precluded by the parallelism of the curves representing the total solids and determined solids.

The same line of argument applies to the fourth theory mentioned above. If the loss of tannin were to be explained by this combination with undetermined solids, the weight of undetermined solids would increase relatively to the weight of total solids. If such a combination is formed, the relative amount of the combining body or complex is so small as to produce no apparent effect on the curves representing the total solids and the determined solids.

We are reduced therefore to the conclusion that the tannin either combines with some substance of very low molecular weight during the ripening of the fruit, or is converted into an insoluble form by a change in the nature of the tannin itself.

The fifth theory seems improbable. If the insolubility of the tannin were produced by a portion of the marc becoming soluble and combining with the tannin while the latter is distributed throughout the fruit, sufficient diffusion after the formation of

[1] U. S. Dept. Agric. Bur. Chem., Bull. 94, p. 42.

the compound to permit its passing to the specialized cells in which it finally collects is improbable. Moreover, the weight of marc would presumably decrease for a time before the tannin becomes insoluble.

It is a matter of great satisfaction to us that just at this point we were able to demonstrate definitely that the tannin itself became insoluble within certain specialized cells of the fruit. It is thus evident that there is no marc accessible with which it can go into combination with the exception of the walls of the particular cells in which it is located. Moreover, as the tannin solidifies it frequently shrinks away from the cell walls, leaving them apparently intact.

The first three theories mentioned above are especially negatived by the fact that the tannin does not disappear from the fruit at any stage, but is left in an insoluble form, and can be rendered soluble by warming with decinormal solutions of acids.

MICROSCOPICAL STUDY OF THE PERSIMMON.

The microscopical study shows that in the early stages of growth of the persimmon the tannin is diffused fairly uniformly throughout the fruit. During its ripening the persimmon flesh softens to an unusual extent. This change is attended as has been shown by the analytical results by a largely increased weight of marc, and a corresponding decrease in the weight of determinable tannin.

Shortly before the softening of the fruit begins, an examination of the fruit shows that the tannin is becoming condensed in certain specialized cells with a corresponding decrease in its occurrence in other parts of the tissue. These cells are often of a larger size than the other cells with which they are associated, but are difficult to differentiate from them by features other than that of size. This condensation of the tannin increases until the cell contents become so firm, owing to the solidification of the tannin, that they break into fragments upon the application of pressure. At this stage it is found that the tannin has all been deposited in these tannin cells.

The characteristic micro-chemical property of the tannin does not seem to have undergone any change, for throughout the whole ripening process, up to and including full ripeness, the tannin gives the characteristic reactions with tannin indicators.

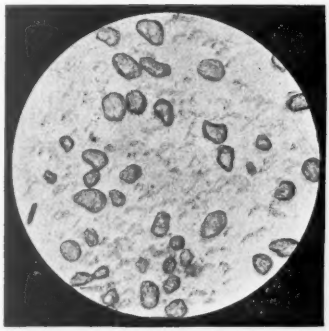


Fig. 1. Tannin cells from ripe American persimmon (*Diospyros Virginiana*). Magnified fourteen times.

Fig. 2. Tannin cells from partially ripe Japanese persimmon (*Diospyros Kaki*) showing the bursting of cell wall and partial discharge of contents by absorption of water. Magnified fourteen times.

Fig. 3. Tannin cells from fully ripe Japanese persimmon, showing characteristic form. Magnified. fourteen times.

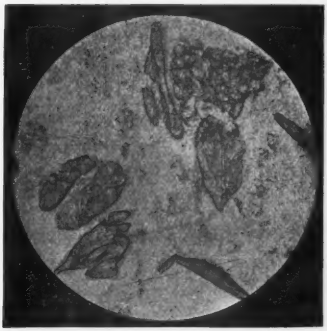


Fig. 4. Tannin cells like those of Fig. 3, but broken into fragments by pressure applied to cover glass. Magnified fourteen times.

The change of the tannin from the perfectly soluble mass diffused uniformly through the fruit to the solid insoluble body isolated in certain cells is very gradual in the growing persimmon, but takes place within a few days after picking, in the stored samples.

The soluble tannin is deposited within the specialized cells where it gradually assumes a jelly-like consistency, and shows an increase in refraction and a decrease in fluidity. If cells from a fruit that has shown softening, be mounted in water, a swelling occurs, and finally a bursting of the cell walls and a discharge of the cell contents into the surrounding media results (Fig. 1). Such swelling and rupturing does not occur after full ripeness has been attained; but instead there results on ripening a solidifying of the cell contents, so that when pressure is applied the cell mass ruptures into fragments. (Fig. 2.) The fact that when a nearly ripe persimmon is eaten the astringent taste is not developed for several seconds after the pulp has been placed in the mouth, finds an interesting explanation in the above experiment, because practically no astringency can be developed until sufficient time has elapsed for the saliva, which is a fluid of low osmotic power, to penetrate the cells, swell and burst them and thus bring the tannin in contact with the nerve terminals.

This phenomenon does not take place if the cells be mounted in the juice of the persimmon, or in any solution of similar or higher osmotic pressure. The size and shape of the tannin cells vary quite widely in the three species, the American, Japanese and Chinese varieties. The cells of two of these, the American and Japanese, are illustrated in Figs. 3 and 4. In the Chinese persimmon the cells are about the size and general shape of those of the American type, but broadly tapering at each end. These features could probably be utilized in determining the kind of pulp used in persimmon fruit products.

The analytical work connected with this article was done by Mr. Gore, and the microscopical work by Mr. Howard.

ON THE EXTRACTION OF FAT FROM FECES AND THE OCCURRENCE OF LECITHIN.

By J. H. Long.

Received April 2, 1906.

In the last few years I have had occasion to carry out a number of experiments on the rapid extraction of fat from feces, and especially with reference to securing enough crude fat for a determination of phosphoric acid as a measure of the lecithin content, or the content of similar phosphorus-holding body. The extraction has been made in the usual manner and also with the use of the paper coil as introduced for the well-known milk test.

When the tests were first made in my laboratory in 1898, I was surprised to find that the results for the crude fat obtained were generally appreciably higher than those obtained by the usual process of drying, grinding with sand and extracting from a paper shell in the Soxhlet apparatus, through the same period. In subsequent work this experience has been repeated, and recently in carefully conducted experiments.

In the paper coil method, as in the other, the moist mass for examination is slightly acidified with very dilute hydrochloric acid to decompose soaps possibly present. Then 10 to 15 grams of the uniformly mixed sample are spread with a spatula over the strip of paper which is finally rolled up, with a piece of extracted cotton twine enclosed, and tied. The coil prepared in this manner dries out quickly to practically constant weight, as may be found by repeated weighings, and in a much shorter time than is required for drying in mass. The dried coil is placed in the Soxhlet apparatus and extracted with anhydrous ether during two days in the usual way; the crude or total fat, including cholesterol, lecithin and some other bodies, is found on evaporation of the ether and may be employed for special examinations. The completion of this extraction requires less time than is necessary for the sand method.

As 10 grams of moist feces yield 2 to 2.5 grams of dry product, usually, the fat secured may weigh from 0.4 to 0.8 gram. In some cases as high as 16 grams of moist feces has been taken, giving an amount of crude fat correspondingly larger. This amount is sufficient for most separations which may be desired. For 1 gram of fat I have frequently found 1.5 mg. P_2O_5 after ignition

of the fat with nitrate and carbonate of sodium, and this in cases where no definite pathological condition could be assumed. The following short table shows something much more remarkable. It exhibits first, the amounts of fat extracted from the same mixed feces by the two methods, and also the phosphorus content of the fat in terms of P_2O_5, which is unusually high for what may be considered as normal feces.

		Coil extraction.			Shell extraction with sand.		
No.	Dry. Per cent.	Fat in dry. Per cent.	P_2O_5 in fat. Per cent.	P_2O_5 in dry. Per cent.	Fat in dry. Per cent.	P_2O_5 in fat. Per cent.	P_2O_5 in dry. Per cent.
1*a*	24.3	28.9	4.15	1.20	27.9	4.73	1.32
1*b*		28.5	..	..	27.5	4.98	1.37
2*a*	19.4	19.5	4.56	0.89	16.2	5.24	0.85
2*b*		18.4	4.77	0.88	16.5	5.02	0.83
3*a*	26.5	30.1	4.38	1.32	29.5	4.20	1.24
3*b*		29.7	4.37	1.29	28.9	4.46	1.29

It appears from the above that the coil extraction yields a larger amount of fat in the three sets of tests. In one case the difference is very marked. It is possible that a much longer treatment here might have increased the yield from the sand extraction. No reason is apparent why such differences should obtain, where sufficient time is given. It must be added that the paper used was found to be perfectly fat-free. The method commends itself on account of ease in manipulation and complete extraction. A perfectly clear ether extract is obtained, which, after evaporation, again dissolves readily in ether.

PHOSPHORUS CONTENT.

Under the conditions of the experiment the ordinary inorganic phosphates can not be extracted with the fat and the phosphoric acid found must evidently be of organic origin, coming possibly from lecithin. But according to all authorities lecithin is found at most in traces only in normal feces. If we calculate the phosphoric acid found above to lecithin it is evident that about half of the crude fat would consist of this body. Assuming the total excretion to be 150 grams, the daily excretion of lecithin on this basis would amount to from 3 to 5.5 grams, about, in the three samples. I could obtain no evidence of the existence of a pathological condition in the man furnishing the material examined. It will be noticed that the phosphoric acid is found in the fat secured

by both methods of extraction, and as pure anhydrous ether was used it can not be traced to substances of inorganic origin.

To further test the matter two other examinations were made some weeks later of the feces of the same individual, apparently still in normal condition. In these tests the paper coil method was followed, in one case with acidification and in the other case without.

The following figures were obtained.

	Dry. Per cent.	Fat in dry. Per cent.	P_2O_5 in fat. Per cent.	P_2O_5 in dry. Per cent.
1 Acidified	23.4	17.8	1.65	0.294
2 No acid		17.6	1.69	0.298

While these results are lower than before in phosphoric acid content, they are still large from the ordinary standpoint. If calculated as lecithin they correspond to an excretion of about 1 gram daily, on the assumption made above as to total excretion.

The amount of lecithin which may be excreted under pathological conditions, or better the amount of organic phosphorus bodies soluble in ether, is relatively large. The results of Deuscher[1] in this regard are remarkable; in the case of a man with closed pancreatic duct as high as 8 grams of lecithin daily was found in the feces, this amount being calculated from the phosphoric acid of the ether extract. With our present knowledge of the distribution of lecithin in animal and vegetable foods it is somewhat difficult to account for such values, or even for the first ones which I reported above. In view of the lack of agreement on this point it appears likely that further attention should be given to the question of the nature of the organic phosphorus compounds which may be extracted from feces by ether. The assumption that these are all of the character of lecithins may not be justified.

NORTHWESTERN UNIVERSITY, March, 1906.

[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY, U. S. DEPARTMENT OF AGRICULTURE. PUBLISHED BY PERMISSION OF THE SECRETARY OF AGRICULTURE. SENT BY H. W. WILEY.]

NOTES ON TYPEWRITER RIBBONS.

BY A. M. DOYLE.

Received March 27, 1906.

IT IS only within comparatively recent years that typewriter

[1] "Jahresbericht über die Fortschritte der Thierchemie," 1898, p. 606; also Schmidt und Strasburger: "Die Faeces des Menschen," p. 160.

machines have been perfected so as to be of practical use. The advantages of such a mechanical contrivance were so great, however, that they were quickly recognized by business men, and the use of the machine has to-day become so general that it has almost completely replaced the old style of longhand writing. Naturally questions have arisen as to the character of the records made, especially as regards permanence. This question was investigated in 1890 by Mr. Thomas Antisell, chemist of the U. S. Patent Office, his results being published in the report of the Commissioner of Public Records of the State of Massachusetts. Other than this report, the writer has been unable to find any literature on the subject of typewriter ribbons.

The Bureau of Chemistry has received requests for information in regard to the character of records made by typewriter ribbons, and these, as well as the need for data to guide in the awarding of contracts, have led the Contracts Laboratory to make the following investigation. The writer is indebted to Mr. L. S. Munson, Chief of the Contracts Laboratory, for many valuable suggestions that were of assistance throughout the work.

Samples were obtained from the Supply Divisions of the various departments and from operators in the Department of Agriculture. The total number of ninety-nine ribbons included fifty-nine new and forty old ribbons representing forty-three brands and nineteen manufacturers. There were 31 record ribbons, mainly black record, and 68 copy ribbons, among which were 30 indelible copy, 11 black copy blue, 12 blue copy, 11 purple copy and four of other kinds.

Operators sending samples of old ribbons were asked to state the length and quality of service rendered by the ribbon, and in this manner information was gathered from a large number of workers. Complaint was made that the ink gummed or smeared; that there was too much ink, clogging the type and making frequent cleaning necessary; that, on the other hand, some ribbons contained an insufficient amount of ink, and therefore did not clog the tpye but were not enduring; that ribbons were unevenly inked, giving spotted writing; that the writing of some ribbons, notably that of the purple copy, faded readily and that the fabric forming the basis of the ribbon wrinkled and stretched along the edges and wore badly in holes.

The length of service as reported varied from less than three weeks to more than seven months, the general idea being that a ribbon should last from six to eight weeks. Very much depends, however, upon the touch of the operator and the action of the machine, as well as the use for which the writing is intended. The amount written by one ribbon was variously reported to be from 264 pages to 2100 pages; the number of words was estimated to be from 109,000 to 630,000, which shows that great differences exist not only in the amount of work done but in the methods of estimating it.

The work of the investigation was conducted along three general lines:

(1) Tests to show the quality of the ribbon fabric—width, total length, weight per square centimeter inked and clean, tensile strength, number of threads in warp and woof and the metric yarn number.

(2) Tests to ascertain the nature of the ink—moisture, ash, lampblack, dye, oil, total inking material and clean ribbon, determining the kind and quantity of each.

(3) Rating of writing and copy on a scale of ten and the action of reagents on the written matter by exposure to sunlight, water, 10 per cent. ammonia, 2 per cent. hydrochloric acid and two-hundredth-normal bleaching-powder.

1. TESTS OF FABRIC.

In the summary which follows the figures were taken from a detailed tabular statement and show the average for each test as well as the variation. The figures for old ribbons in width, length, number of threads and yarn number were about the same as for new ribbons and were, therefore, included among them.

The varying widths of ribbons adapt them for use on different machines. In all totals, medium width ribbons were included among wide ribbons. In length, wide ribbons varied from nineteen feet to one-half as much more and narrow ones ranged from twenty-nine feet to nearly twice the amount, the averages being 25.5 and 42.8 feet respectively.

Considering the weight per square centimeter, the weight of the inked ribbons, both new and old, varied as much as one-third of the average weight; the weight of the clean ribbons varied

NEW RIBBONS.

Kind of test.	Kind of ribbon.	Number of samples.	Unit of measure.	Variation.	Average.
Width	Wide	61	cm.	3.4 – 3.8	....
	Medium	7		2.4 – 2.6	....
	Narrow	31		1.0 – 1.2	....
Total length	Wide	68	ft.	19.00–28.50	25.50
	Narrow	31		29.50–54.50	42.80
Weight, sq. cm., inked	Record	20	mgm.	8.50–11.76	9.80
	Copy	39		7.26–11.68	9.49
Weight, sq. cm., clean	Record	20	mgm.	5.58–8.76	6.47
	Copy	39		4.79– 7.62	6.15
Tensile strength	Wide	35	lbs.	26.50–50.30	38.80
	Narrow	20		11.70–27.80	20.60
Number of threads	Wide	48	..	48×43–58×56	54×52
	Narrow	28	..	50×49–63×47	59×45
Metric yarn number	Wide	48	..	50– 105	85
	Narrow	28	..	65– 110	85

OLD RIBBONS.

Weight, sq. cm., inked	Record	11	mgm.	8.21–11.37	10.11
	Copy	29		7.55–11.47	9.42
Weight, sq. cm., clean	Record	11	mgm.	5.88– 8.59	7.61
	Copy	29		4.89– 8.23	6.62
Tensile strength	Wide	14	lbs.	16.50–39.10	27.10
	Narrow	6		11.50–22.70	19.50

as much as one-half of the average weight; and these variations were as much or greater than the total amount of the ink, found by taking the difference between the totals for inked and clean ribbons, that is, the average weight of ink was found to be about one-third the weight of the ribbon, and the variation among different ribbons equaled or even exceeded the weight of ink. The average weight of the inked ribbon differed very little whether the ribbon was old or new. The averages for 59 new and 22 old ribbons, eliminating certain abnormal figures which appear in the above totals, were 9.60 and 9.34 mg. per sq. cm. respectively. Inasmuch as all of the old ribbons were reported by operators to be in an exhausted condition, it would appear that the exhaustion of a ribbon depends more upon the wear of the fabric than upon the amount of ink removed. In connection with the

weight per square centimeter, the evenness of the inking was tested by comparing the weights of ten or more sections of the same ribbon. The strips, which were about 35 cm. long, weighed approximately 1 gram, and were found to vary as much as 10 per cent. of the average weight. Shorter lengths would probably have shown greater differences.

The summary which follows shows the variation and averages of the weights per square centimeter for the products of the same factory:

Number of samples from one manufacturer.	Variation, inked ribbon.	Per cent.	Variation, clean ribbon.	Per cent.	Average.	
					Inked.	Clean.
31	7.97–10.02	23	4.93–6.29	23	8.92	5.90
16	8.51–11.68	30	6.08–8.23	30	10.63	7.17
12	8.98–10.74	18	6.18–7.90	25	9.86	6.93
11	8.50–10.75	24	4.96–6.18	21	9.26	5.72

The variation, calculated on the average weight, ranged in the inked ribbon from 18 to 30 per cent. and in the clean ribbon from 21 to 30 per cent. The variation for clean ribbon, therefore, was equal to or greater than that for the inked ribbon, which would seem to show that the ribbon fabric varies rather than the quantity of ink. In the last line, where an exception may be noted, the eleven samples were obtained at the same time from the manufacturer, and there was noticeably less variation in the strength of the material as determined by the tensile strength tests. It is possible, therefore, that a part of the variation may be due to the varying ages of the ribbons, but, aside from this, it is evident that the weight of the material employed by manufacturers is far from being uniform.

The figures for tensile strength represent each an average of at least ten, frequently twelve or fifteen determinations. One inch of the ribbon was tested at a time and so great were the differences between sections that a fair average was obtained only by a large number of tests. Many of the ribbons showed differences of as much as seven and one-half pounds in successive tests on the same ribbon, while the maximum difference for the same ribbon was twelve pounds. Comparing different ribbons, some bore fully twice the strain of others in the same class. Old ribbons, as might be expected, were of less strength, the total difference being marked in the case of wide ribbons but obscured in the total for narrow ribbons because of the presence of selvage.

The number of threads, warp and woof, and the metric yarn number were ascertained by Mr. B. J. Howard, Chief of the Microscopic Laboratory. The number of threads, which were directly counted under a microscope with micrometer attachment, together with the weight per square centimeter of the clean ribbon, gave the yarn number, according to a formula worked out by Herzfeld.[1] The number of threads, yarn number and tensile strength would naturally be closely related but the results did not establish such relation, possibly because the date of manufacture was not considered. Ribbons may become weak and even fall to pieces in time, owing to the presence of corrosive materials in the ink, and it is, therefore, probable that the apparent lack of agreement in the three sets of figures is due to the fact that the ribbons had been on hand for a greater or less length of time.

2. TESTS OF INK.

Kind of test.	Number of samples. New.	Number of samples. Old.	Variation, both new and old. Per cent.	Average. New. Per cent.	Average. Old. Per cent.	Average. Total. Per cent.
Moisture, or matter volatile at 100° C..	59	40	2.67– 6.06	4.28	3.68	4.05
Ash.....	58	22	0.43–15.24	2.48	1.82	2.27
Lampblack, record..	18	8	0.88– 7.00	3.18	2.32	3.03
Lampblack, copy.....	22	18	0.25– 3.44	1.57	1.54	1.56
Dye.....	31	...	3.34– 9.26	5.85	.....	5.85
Oil.....	59	22	15.43–31.02	22.09	19.40	21.26
Total ink	58	40	20.56–46.00	34.78	28.42	33.38
Clean ribbon.....	58	40	79.44–54.00	65.22	71.58	66.62

In the summary of the tests for the ink, the averages for the new and old ribbons were separated, but the variation differences were not great enough to make two statements necessary. In all of the tests the variation among ribbons, both new and old, was very wide. The volatile matter, determined by heating to constant weight at 100° C., averaged about six-tenths lower in old ribbons, showed practically no variation from day to day, but lessened gradually as the ribbon aged. The ash, which was determined by burning off carbonaceous matter at a low red heat, varied in general between 1 and 2 per cent. From 3 to 5 per cent. is a high ash content, and above 5 per cent. is very unusual. The kind and quantity of ash give valuable indications of the coloring-matter used for the ink.

[1] See "Yarns and Textile Fabrics."

The determination of the lampblack was very difficult because it was almost impossible to separate it from the fibres of the ribbon. Of the several methods tried, but two gave any measure of success and these agreed only within two or three-tenths of a per cent. In one method the cotton material was dissolved away by strong sulphuric acid, and the resulting solution passed through a Gooch filter which retained the lampblack. The other method consisted in separating the lampblack mechanically, in ethereal and alcoholic solution, by shaking and rubbing, the carbon being collected on a Gooch crucible. The latter method allowed of a direct weighing of the cotton skeleton of the ribbon and for this reason was the preferred method. All of the black record, black-copy-blue and indelible copy ribbons contained lampblack, copy ribbons averaging about 1.5 per cent., and record ribbons about twice as much.

On treating the ribbon with ether to extract the oil and filtering through a Gooch crucible, it frequently happened that the dye, as well as the carbon, was filtered out. After removal of all of the oil by ether, the ribbon and crucible were both dried and weighed. They were then treated with alcohol and water, and sometimes strong acid, which removed the dye, and, after drying and again weighing, the dye was found by difference. This method gave excellent results. Methylene blue, which was very commonly used, was determined by titration with a standard solution of Krystal Ponceau, according to a method worked out by E. Pelet and V. Garuti, published in the *Bulletin de la Soc. Chim. de Paris*. Duplicate tests agreed within 0.05 per cent. The summary gives the results of 31 determinations of methylene blue made by this method.

The oil was determined by extraction with ether and direct weighing. The amount of oil, which appears to influence the working qualities materially, averaged about 22 per cent. Much less shortens the life of the ribbon, and much more clogs the type and makes the writing blurred, while the length of service is not correspondingly increased.

The figures for total writing material equal the difference between 100 per cent. and the total clean ribbon. Not a very close relation seems to exist between total ink and ribbon efficiency, although as a rule those ribbons having high working qualities possessed more than the average amount of ink, made up of more

than average content of oil and dye. The total ink of ribbons of a popular make ranged from 27 to 38 per cent., showing that wide variation is possible in ribbons giving general satisfaction. Ribbons of much less than average ink may possess good working qualities for a time but they do not last well. Those with low percentage of either dye or oil seldom work well and low amounts of lampblack detract from the permanence of the writing. The percentage of available ink was roughly determined by taking short pieces of the ribbons, weighing, using to the point of exhaustion and again weighing. Of the 27 ribbons thus treated, the loss ranged from 1.8 per cent. to 16.5 per cent. with an average of 8.0 per cent. calculated on the actual space exhausted. This agrees very well with an average loss of about 6 per cent. of the total ribbon, shown in the summary of tests. The ribbons yielding the greatest amount of available ink, in the above test, did not as a rule give a larger amount of writing, but rather showed a tendency to clog the type and blur the writing, showing that the ink flowed too freely. One ribbon wrote twice the number of lines that any other ribbon was able to do, and contained 13.5 per cent. of available ink. This ribbon contained high percentages of moisture and of dye but only average amounts of the other ingredients. It is to be regretted that but one of this make of ribbon was examined.

3. TESTS OF WRITING.

In the rating of the writing and the copy, the best was assumed as a standard, ranked one, and the other figures up to ten show a gradation from clear, strong impressions to writing that is barely legible. The effect of reagents was also rated on a scale of ten, ranging from one, or "unaffected" to ten, or "completely effaced." In all of the tests the uncopied writing, the copied writing and the copy were similarly treated. The sunlight test, which was very severe, consisted in exposing the three kinds of writing, under glass, to the direct rays of the sun for ten days. Very weak solutions of the wet reagents were employed, but these, too, proved to be rather severe when applied for twenty-four hours. In a general way it was found that in treatment with reagents the original writing was severely attacked, the copied writing was less so and the copy was completely effaced. With few exceptions record ribbons furnished permanent records and the

original writing of those copy ribbons that contained lampblack was permanent, but the copies were not. Copy ribbons failed to give indelible copies because almost none of the carbon was transferred. On exposure of the copy to sunlight for ten days or less, the dye faded out completely, leaving the writing illegible. Most of the ribbons were very satisfactory when fresh, both the original and the press copy being good, but marked differences in the quality of the records were developed by wear, a number which gave good results at first being quickly exhausted.

From the foregoing it may be seen that ribbons of different makes differ widely in their properties; that ribbons of the same make differ as widely; that the ribbon itself is of uneven construction; that the fabric, more than the ink, is the cause of these variations; that many record ribbons furnish permanent records and that much is yet to be desired in the attainment of truly indelible copy ribbons. It is evident that there is need for definite requirements to regulate the purchase of typewriter ribbons, especially as regards the material which is employed as a basis for the ink. An essential of a good ribbon is that the fabric be of the quality best fitted to endure the special kind of service required until all ink available for good writing is exhausted.

AN ANALYSIS OF THE WATER OF DEATH GULCH.

By G. B. FRANKFORTER.

Received February 7, 1906.

PROBABLY no other spot of the same area in the whole world furnishes such a wealth of natural waters as our Yellowstone National Park. Within its bounds may be found waters containing carbonic acid gas, silicic, boric, sulphuric, hydrosulphuric and even free hydrochloric acid, in addition to salts of nearly all of the metals ever found in any natural water.

One of the most remarkable waters in the park is that of the little stream which flows down through a narrow ravine into Cache Creek. This ravine is now known as Death Gulch. It was discovered by Walter H. Weed in 1888 while exploring for the United States Geological Survey and fully described by him in *Science*. In 1898 it was visited by Dr. Jaggar who found in the gulch the remains of a number of animals including seven

grizzlies. Later, it was visited by Captain Critenden who found no remains of animals nor evidences of obnoxious gases. In 1898 Lieut. Lindley found the remains of several bears and indications of gases which produces dizziness and headache. F. W. Traphagen also visited the gulch and found the remains of bears and other animals. He made an examination of the air and found a large amount of carbon dioxide, and the gas which escaped from a crevice contained about 1 per cent. of hydrogen sulphide and more than 50 per cent. of carbon dioxide.

Death Gulch is located in the extreme northeastern part of the park on the Cache Creek about two miles above its confluence with the Lamar river. Owing to inaccessibility, comparatively few persons have visited it. My attention was called to it several years ago while visiting the park but being completely out of the tourists' route, I was unable to visit it. However, Mr. A. D. Hall, a geologist who has spent every summer for a number of years in the park and explored almost every foot of ground, visited the gulch several times. He had no difficulty in recognizing the gulch from the description of those who had visited it before him, but more easily was it recognized by a number of carcasses of bears and other animals which had perished by poisoning, either from gas or water, presumably the former.

Mr. Weed describes the gulch as a simple V-shaped trench not over seventy-five feet deep, cut in the mountain slope and not a hollow or cave. That the gas at times accumulates in the pocket at the head of the gulch, is, however, proved by the dead squirrels, etc., found on its bottom. Having made tests for carbonic acid gas with negative results, Mr. Weed says:

"It is not probable that the gas ever accumulates to a considerable depth, owing to the open nature of the place and the fact that the gulch draining it would carry off the gas which would, from its density, tend to flow down the ravine." Mr. Hall likewise questions the accumulation of any great amount of gas in the gulch and gives as an additional reason the rapid diffusion of the heavy gas with the air, caused by the wind blowing up the gulch. The rocks through which the stream has cut its way are described as volcanic, partially disintegrated and apparently filled with sulphur. The bed of the stream is estimated as having a declination of about 40°, and the sides of the gulch an average of not over 60°. Mr. Hall states that he failed

in every visit to recognize the slightest odor of hydrogen sulphide. However, animals which were placed in the gas as it escaped from the crevices in the rocks, perished in a short time.

While there can be no doubt concerning the escape of obnoxious gases from the crevices in the rocks, it was nevertheless thought, from the above topography and the fact that gases could not accumulate in large quantities as in the case of Death Valley, in Java and Grotto del Cane, near Naples, that the water in the gulch might possibly play a part in making the gulch a natural bear trap. Samples of water were therefore collected at various times and examined. They were found to vary widely, depending upon the quantity of water in the gulch. In the spring when the snow is melting and the little stream becomes a good-sized mountain creek, the water is entirely different from that found in the gulch in the fall. In late summer, the stream is almost dry.

The sample of water, an analysis of which appears below, was collected in August 1903. It was taken from a pool near which were crevices in the rocks and from which a perfectly odorless gas escaped. The water was strongly acid.

An analysis gave the following:

	Grams per liter.
SiO_2	0.8100
Al	1.9438
Fe	8.3173
Ca	0.3142
Mg	0.0080
Na	0.9069
K	0.1489
SO_4	42.2904
Cl	1.0326
	55.7721

When collected, the sample had a peculiar yellowish green color. After standing several months it became darker in color and somewhat resembled commercial sulphuric acid. At the time of the analysis, the iron was all in the ferric form. After two years, a further change had apparently taken place. The specific gravity was a little less, being 1.05156, and there was a deposit in the bottom of the bottle. This precipitate was examined and found to be composed almost wholly of free sulphur and silica. In discussing this matter with Mr. Hall who collected the sample, it was found that most of this precipitate was sus-

pended matter at the time of the taking of the sample, but owing to the finely divided state and the dark color of the water it escaped notice unless the sample stood quietly for some time. The bottom of the pool was covered with this precipitate or milk of sulphur. It is therefore possible that it may have come from hydrogen sulphide, although there was no evidence of the presence of the gas when the sample was taken. Tests for the presence of arsenic and the rare elements gave negative results.

UNIVERSITY OF MINNESOTA, MINNEAPOLIS.

VAPOR-PRESSURE AND CHEMICAL COMPOSITION.

BY EUGENE C. BINGHAM.

Received March 27, 1906.

ACCORDING to the theory of corresponding conditions, the calculation of the vapor-pressure curve is possible by means of some equation of the form

$$\frac{p}{\pi} = \int\left(\frac{T}{\tau}\right)$$

where π and τ represent the critical pressure and critical temperature respectively. $\int\left(\frac{T}{\tau}\right)$ is then a temperature function which is independent of the nature of the substance under consideration. Van der Waals[1] gave, as a first approximation to this function, the form

$$\log \frac{\pi}{p} = a\left(\frac{\tau}{T} - 1\right) \quad . \quad . \quad . \quad (1)$$

where a has the same value for all substances. Van der Waals found this to be about 3.0. Considering the simplicity of the formula, the approximation is remarkable; yet the values of a are not the same for different substances and the values vary somewhat also with the temperature.

To investigate this point more fully Nernst[2] plotted curves for a number of substances, using values of $\log \frac{\pi}{p}$ as ordinates and of $\frac{\tau}{T} - 1$ as abscissae. It was found that the slope of the curves increases quite regularly with the molecular weight of the substances. It is at least apparent that the curves of all substances do not fall together into a single straight line as the theory of

[1] Kontinuität, p. 148.

[2] Nachrichten Kgl. Ges. Wiss. Göttingen, 1906.

corresponding condition demands. Moreover, the curves of substances of very small molecular weight, bend toward the X-axis as the values of $\frac{\tau}{T} - 1$ increase while those of the substances of large molecular weight bend in the opposite direction. Following the suggestion of Prof. Nernst I have plotted curves for a large number of substances and have found the same characteristics present.

Even if the function $\int\left(\frac{T}{\tau}\right)$ is not *the same* for all substances, it may be of the same *nature* for all, only having different numerical constants, from substance to substance. The vapor-pressure curve, in this case, would be determined when we knew the critical temperature and pressure and in addition a single point of the vapor-pressure curve as, for example, the boiling-point. Nernst[1] has given as an expression of this function the form

$$ln\ \frac{\pi}{p} = m\ ln\ \frac{\tau}{T} + \alpha'\left[\left(\frac{\tau}{T} - 1\right) - \frac{1}{n}\left(1 - \frac{T}{\tau}\right)\right]$$

where m and n are constants for all substances and α' a constant varying with the nature of the substance. I have given considerable effort to finding the best values for these constants and to trying the effect of adding another term, but have found no form more satisfactory than that given by Nernst as cited above,

$$\log\ \frac{\pi}{p} = 1.75\ \log\ \frac{\tau}{T} + \alpha'\left[\left(\frac{\tau}{T} - 1\right) - \frac{1}{2.36}\left(1 - \frac{T}{\tau}\right)\right] \quad (2)$$

Since $\alpha'\left(\frac{\tau}{T} - 1\right)$ is the most important term, the above equation is seen to be a development of Van der Waals' equation (1). Indeed, for medium values of α' the terms $1.75\ \log\ \frac{\tau}{T}$ and $\frac{\alpha'}{2.36}\left(1 - \frac{T}{\tau}\right)$ nearly counteract each other. There are deviations in the region of the critical temperature, but we can only expect equation (2) to hold at low temperatures where the vapor obeys the gas laws.

In the following tables the values of α' and of $M\alpha'$ (where M is the molecular weight) are given for a large number of substances as calculated from the temperature of their boiling-points under atmospheric pressure and the critical date.

In order to show the regularities inherent in these values,

[1] Loc. cit.

"atomic" values for each element have been calculated, the substance used for this purpose being enclosed in brackets in Table I. The value for carbon is a mean value, approximately that of pentane. From the atomic values, the molecular values, $M\alpha'$, for the different compounds are calculated by addition and compared with the observed values. Thus, if any compound is represented by the formula

$$C_lH_mO_nN_oS_pF_qCl_rBr_sI_tAr_uKr_vXe_wGe_xSe_ySn_z$$

where l, m, n, ...are the number of atoms of carbon, hydrogen, oxygen, ...respectively in the molecule, then

$$M\alpha' = 42l + 1.9m + 41n + 34.4o + 85p + 46q + 98r + 236s + 381t + 85.4u + 195v + 297w + 306x + 201y + 460z \ldots . \quad (3)$$

The agreement is perhaps as good as we ought to expect. The differences among the isomers are partly due to constitutive influences which have not been taken into account in the formula. In the series of aliphatic hydrocarbons, the observed values of $M\alpha'$ increase more rapidly than those calculated by the formula. This is reminiscent of the effect of constitutive influences which is met with in considering the molecular volumes[1] of these substances. Further, it is certain that equation (2) is only a rough approximation so it is sufficient for the present to have shown that these quantitative constitutive influences are present.

TABLE I.[2]

Substance.	Formula.	M.	π atm.	τ abs.	α'.	$M\alpha'$.	$M\alpha'$ calc.	Diff.
Hydrogen	H_2	2.0	14.2	32.2	1.92	3.8	[3.8]	
Argon	Ar	39.9	52.9	155.6	2.14	85.0	[85.]	
Methane	CH_4	16.0	55.2	191.2	2.26	36.0	50	—14
Xenon	Xe	128.0	57.2	287.8	2.32	297	[297]	
Carbon monoxide	CO	28.0	35.5	137.4	.....	.....	.....	
Krypton	Kr	81.8	54.3	210.5	2.38	195	[195]	
Nitrogen	N_2	28.1	27.5	124.0	2.45	69	[69]	
Hydrogen selenide	H_2Se	81.2	91.0	411.0	2.52	205	[205]	
Oxygen	O_2	32.0	50.8	154.2	2.55	82	[82]	
Chlorine	Cl_2	70.9	93.5	419.0	2.77	196	[196]	
Carbon disulphide	CS_2	76.1	77.8	548.0	2.79	212	[212]	
Carbon tetrachloride	CCl_4	153.8	44.97	556.15	2.99	460	435	25
Ammonia	NH_3	17.1	107.6	404.0	3.02	52	41	11
Benzene	C_6H_6	78.0	47.89	561.5	3.07	239	263	—24
Hexamethylene	C_6H_{12}	84.1	39.82	552.95	3.08	259	275	—16
Diisopropyl	C_6H_{14}	86.1	30.72	500.4	3.19	275	279	— 4

[1] Van't Hoff: Theoretische Chemie, Vol. III, p. 32, 2d ed.

[2] Landolt and Börnstein's tables.

TABLE I—*Continued.*

Substance.	Formula.	M.	π atm.	τ abs.	α'.	$M\alpha'$.	$M\alpha'$ calc.	Diff.
Pentane	C_5H_{12}	72.1	33.03	470.2	3.21	231	233	— 2
Phenyl iodide	C_6H_5I	204.0	42.62	721.0	3.15	643	[643]	
Phenyl chloride	C_6H_5Cl	112.5	44.62	633.0	3.18	358	360	— 2
Phenyl fluoride	C_6H_5F	96.1	44.62	559.6	3.20	308	[308]	
Methyl formate	$C_2H_4O_2$	60.0	59.24	487.0	3.22	193	173	20
Stannic chloride	$SnCl_4$	260.8	36.95	591.7	3.27	853	[853]	
Ether	$C_4H_{10}O$	74.1	35.61	467.4	3.29	244	228	16
Hexane	C_6H_{14}	86.1	29.62	507.8	3.38	291	279	12
Acetone	C_3H_6O	58.0	60.0	510.5	3.53	205	223	—18
Water	H_2O	18.0	194.6	638.0	3.80	68	45	23
Ethyl acetate	$C_4H_8O_2$	88.1	37.94	523.1	3.61	318	265	53
Acetic acid	$C_2H_4O_2$	60.0	57.11	594.6	3.85	231	173	58
Methyl butyrate	$C_5H_{10}O_2$	102.1	34.21	554.25	3.66	374	311	63
Octane	C_8H_{18}	114.1	24.70	569.2	3.69	421	370	51
Methyl alcohol	CH_4O	32.0	78.63	513.0	4.22	135	90	45
Ethyl alcohol	C_2H_6O	46.0	62.76	516.6	4.50	207	136	71
Propyl alcohol	C_3H_8O	60.1	50.16	536.7	4.45	267	182	85
Isobutyl alcohol	$C_4H_{10}O$	74.1	48.27	538.0	4.87	361	228	133

TABLE II.

Substance.	Formula.	M.	π atm.	τ abs.	α'.	$M\alpha'$.	$M\alpha'$ calc.	Diff.
Methane	CH_4	16.0	55.2	191.2	2.26	36	50	—14
Ethane	C_2H_6	30.0	45.2	308.0	2.47	74	95	—21
Ethylene	C_2H_4	28.0	53.5	282.8	2.76	77	92	—15
Propane	C_3H_8	44.1	44.	370	3.14	138	141	— 3
Pentane	C_5H_{12}	72.1	33.03	470.2	3.21	231	233	— 2
Isopentane	C_5H_{12}	72.1	32.92	460.8	3.22	232	233	— 1
Isoamylene	C_5H_{10}	70.1	33.9	464.6	3.34	234	229	5
Benzene	C_6H_6	78.0	47.89	561.5	3.07	239	263	—24
Hexamethylene	C_6H_{12}	84.1	39.82	552.95	3.08	259	275	—16
Hexane	C_6H_{14}	86.1	29.62	507.8	3.38	291	279	12
Diisopropyl	C_6H_{14}	86.1	30.72	500.4	3.19	275	279	— 4
Toluene	C_7H_8	92.1	41.6	593.6	3.22	297	309	—12
Heptane	C_7H_{16}	100.1	26.86	539.9	3.66	366	324	42
Xylene	C_8H_{10}	106.1	36.9	631.3	3.30	350	355	— 5
Xylene	C_8H_{10}	106.1	35.8	618.6	3.46	367	355	12
Xylene	C_8H_{10}	106.1	35.0	617.4	3.40	361	355	6
Ethylbenzene	C_8H_{10}	106.1	38.1	619.4	3.36	356	355	1
Diisobutyl	C_8H_{18}	114.1	24.55	549.8	3.58	408	370	38
Octane	C_8H_{18}	114.1	24.70	569.2	3.69	421	370	51
Mesitylene	C_9H_{12}	120.1	33.2	640.7	3.75	450	401	49
Propylbenzene	C_9H_{12}	120.1	32.3	638.6	3.50	420	401	19
Isopropylbenzene	C_9H_{12}	120.1	32.2	635.7	3.41	410	401	9
Pseudocumol	C_9H_{12}	120.1	33.2	654.2	3.60	432	401	31
Naphthalene	$C_{10}H_8$	128.1	39.2	741.2	3.50	448	435	13
Durene	$C_{10}H_{14}$	134.1	28.6	675.5	3.58	480	447	33
Isobutylbenzene	$C_{10}H_{14}$	134.1	31.1	650.1	3.54	475	447	28

TABLE II—*Continued.*

Substance.	Formula.	M.	π atm.	τ abs.	α'.	$M\alpha'$.	$M\alpha'$ calc.	Diff.
Decane	$C_{10}H_{22}$	142.2	21.3	603.4	4.55	647	462	185
Diphenyl	$C_{12}H_{10}$	154.1	31.8	768.6	3.74	576	523	53
Diphenylmethane	$C_{13}H_{12}$	168.1	28.2	770.0	3.94	662	567	95

TABLE III.

Substance.	Formula.	M.	π atm.	τ abs.	α'.	$M\alpha'$.	$M\alpha'$ calc.	Diff.
Methylamine	CH_5N	31.1	72.0	428.0	3.37	105	86	19
Dimethylamine	C_2H_9N	45.1	56.0	436.0	3.49	157	132	25
Trimethylamine	C_3H_9N	59.1	41.0	433.5	3.07	181	178	3
Ethylamine	C_2H_7N	45.1	66.0	450.0	3.79	171	132	39
Diethylamine	$C_4H_{11}N$	73.1	39.3	491.0	2.63	192	223	—31
Triethylamine	$C_6H_{15}N$	101.2	30.0	532.0	3.51	355	315	40
Propylamine	C_3H_9N	59.1	50.0	491.0	3.67	217	178	39
Dipropylamine	$C_6H_{15}N$	101.1	31.0	550.0	3.94	398	315	83
Aniline	C_6H_7N	93.1	52.35	698.7	3.65	340	300	40
Dimethylaniline	$C_8H_{11}N$	121.1	35.8	687.45	3.71	449	391	58
Dimethylorthotoluidine	$C_9H_{13}N$	135.1	30.8	667.8	3.65	493	437	56
Propionitrile	C_3H_5N	55.1	41.3	558.7	3.55	196	170	26
Butyronitrile	C_4H_7N	69.1	37.4	582.1	3.67	254	216	38
Capronitrile	$C_6H_{11}N$	97.1	32.15	621.8	3.77	366	307	59
Benzonitrile	C_7H_5N	103.1	41.6	699.0	3.59	370	338	32
Nitrous oxide	N_2O	44.1	74.0	308.9	2.86	126	110	16
Nitric oxide	NO	30.0	71.2	179.5	4.36	131	75	56

TABLE IV.

Substance.	Formula.	M.	π atm.	τ abs.	α'.	$M\alpha'$.	$M\alpha'$ calc.	Diff.
Methyl chloride	CH_3Cl	50.5	73.0	414.5	2.99	151	146	5
Chloroform	$CHCl_3$	119.4	54.9	533.0	3.17	379	338	41
Carbon tetrachloride	CCl_4	153.8	44.97	556.15	2.99	460	435	25
Ethylene chloride	$C_2H_4Cl_2$	98.9	53.0	561.4	3.28	324	288	36
Ethylidene chloride	$C_2H_4Cl_2$	98.9	52.4	528.0	3.19	316	288	28
Propyl chloride	C_3H_7Cl	78.5	49.0	494.0	3.43	269	238	31
Phenyl chloride	C_6H_5Cl	112.5	44.62	633.0	3.18	358	360	— 2
Germanium tetrachloride	$GeCl_4$	214.3	38.0	549.9	3.26	699	[699]	
Ethylene bromide	$C_2H_4Br_2$	188.0	70.6	582.8	5.05	950	735	215
Thiophene	C_4H_4S	84.1	47.7	590.3	2.67	225	261	—36

TABLE V.

Substance.	Formula.	M.	π atm.	τ abs.	α'.	$M\alpha'$.	$M\alpha'$ calc.	Diff.
Methyl formate	$C_2H_4O_2$	60.0	59.35	487.0	3.22	193	173	20
Ethyl formate	$C_3H_6O_2$	74.1	46.83	508.3	3.30	244	219	25
Propyl formate	$C_4H_8O_2$	88.1	40.05	537.85	3.43	302	265	37
Amyl formate	$C_6H_{12}O_2$	116.1	34.12	575.6	4.20	488	356	132
Methyl acetate	$C_3H_6O_2$	74.1	46.29	506.7	3.47	257	219	38
Ethyl acetate	$C_4H_8O_2$	88.1	37.94	523.1	3.61	318	265	53
Propyl acetate	$C_5H_{10}O_2$	102.1	33.17	549.2	3.74	382	311	71

TABLE V—*Continued.*

Substance.	Formula.	M.	π atm.	τ abs	α'.	$M\alpha'$.	$M\alpha'$ calc.	Diff.
Isobutyl acetate	$C_6H_{12}O_2$	116.1	31.4	561.3	3.92	455	356	99
Methyl propionate...	$C_4H_8O_2$	88.1	39.51	530.4	3.56	314	265	49
Ethyl propionate.....	$C_5H_{10}O_2$	102.1	33.17	545.9	3.71	379	311	68
Methyl butyrate.....	$C_5H_{10}O_2$	102.1	34.21	554.25	3.66	374	311	63
Ethyl butyrate.....	$C_6H_{12}O_2$	116.1	30.24	565.8	3.88	451	356	94
Methyl isobutyrate..	$C_5H_{10}O_2$	102.1	33.88	540.55	3.61	369	311	58
Ethyl isobutyrate....	$C_6H_{12}O_2$	116.1	30.13	553.4	3.82	444	356	88
Methyl valerate.....	$C_6H_{12}O_2$	116.1	31.5	566.7	4.23	491	356	135

TABLE VI.

Substance.	Formula.	M.	π atm.	τ abs.	α'.	$M\alpha'$.	$M\alpha'$ calc.	Diff.
Methyl ether.....	C_2H_6O	46.1	57.0	402.6	3.07	142	136	6
Methyl ethyl ether...	C_3H_8O	60.1	46.27	441.4	3.28	197	182	15
Ether	$C_4H_{10}O$	74.1	35.61	467.4	3.29	244	228	16
Acetone	C_3H_6O	58.0	60.0	510.5	3.53	205	223	—18
Methyl alcohol.....	CH_4O	32.0	78.63	530.5	4.22	135	90	45
Ethyl alcohol.....	C_2H_6O	46.0	62.76	516.6	4.50	207	136	71
Propyl alcohol.....	C_3H_8O	60.1	50.16	536.7	4.45	267	182	85
Isopropyl alcohol.....	C_3H_8O	60.1	53.1	507.6	4.91	295	182	13
Isobutyl alcohol.....	$C_4H_{10}O$	74.1	48.27	538.0	4.87	361	228	133
Cresol.....	C_7H_8O	108.1	45.0	705.0	3.94	426	350	76
Anisol	C_7H_8O	108.1	41.25	641.5	3.62	395	350	45
Water.....	H_2O	18.0	194.6	638.0	3.80	68	45	23
Acetic acid..	$C_2H_4O_2$	60.0	57.11	594.6	3.85	231	173	58
Carbon dioxide.....	CO_2	44.0	72.9	304.35	3.15	139	124	15
Sulphur dioxide.....	SO_2	64.1	78.9	428.4	3.27	210	167	53

In Table I the substances are grouped according to the values of α'. It is seen that the elements of small molecular weight as hydrogen have the smallest values of α' and that they increase regularly up to the alcohols of high molecular weight and considerable association. Table II contains a large number of hydrocarbons grouped according to their complexity. Table III contains nitrogen compounds—amines, nitriles, and oxides of nitrogen. Table IV contains various halogen and sulphur compounds, while in Table V are grouped the esters, and in Table VI alcohols, acids and other oxygen compounds. In the associated compounds there is wide divergence between the observed and calculated values of $M\alpha'$.

CONCLUSION.

From the study of a large number of substances, Nernst's[1] equation

[1] Loc. cit.

$$\log \frac{\pi}{p} = 1.75 \log \frac{\tau}{T} + \alpha' \left[\left(\frac{\tau}{T} - 1 \right) - \frac{1}{2.36} \left(1 - \frac{T}{\tau} \right) \right]$$

was found to agree satisfactorily with the results of observation. The values of α' have been determined for as many substances as possible. The values are found to increase quite regularly in proportion to the complexity of the molecule, being smallest for hydrogen and the monatomic gases and greatest for the associated alcohols of high molecular weight. It has been shown that these values may be represented by an equation

$$M\alpha' = 42l + 1.9m + 41n + \ldots\ldots$$

where M is the molecular weight of the substance and l, m, n, ... are the number of atoms of the elements, carbon, hydrogen, oxygen, ... respectively in the molecule.

BERLIN, March, 1906.

THE RELATION OF HEAT OF VAPORIZATION TO BOILING-POINT.

BY EUGENE C. BINGHAM.

Received March 27, 1906.

TROUTON'S rule states that the quotient of the molecular heat of vaporization divided by the absolute temperature of the boiling-point is a constant. This has been accepted as approximately true for normal substances. Acetic acid, however, gives an abnormally small value, which is accounted for by van't Hoff[1] by the fact that the molecules of acetic acid are largely associated both in the liquid and vapor, which would cause the true molecular heat of vaporization to be much larger than the one found. In the case of ethyl alcohol, the vapor is normal but the liquid is associated, so the breaking down of association being connected with an absorption of heat accounts for the abnormally high value of this substance.

More recently Nernst[2] has pointed out that even among unassociated compounds, the values of this quotient increase considerably with the temperature, if we only choose substances boiling at widely different temperatures. Nernst gave, as a closer approximation to the true values, the equation:

$$\frac{\lambda'}{T_o} = 8.5 \log T_o,$$

[1] Theor. Chemie, Vol. III, p. 54, 2d ed.

[2] Nachrichten Kgl. Ges. Wiss. Göttingen, 1906.

where T_0 is the boiling-point and λ' the molecular heat of vaporization.

This approximation is shown by the following table taken from Nernst's paper:[1]

TABLE I.

Substance.	$\frac{T_1+T_2}{2}$	$\frac{\lambda}{1-\frac{p}{\pi}}$	T_0.	λ' calc.	λ' obs.	$\frac{\lambda'}{T_0}$	8.5 log T_0.
Hydrogen	20.4	229	20.4	213	.....	10.4	11.1
Hydrogen	18.1	234					
Nitrogen	76.7	1428	77.5	1386	1334	17.9	16.1
Nitrogen	73.9	1446					
Argon	87.1	1445	87	1418	.....	16.3	16.5
Oxygen	90.1	1692	90.6	1660	1629	18.3	16.7
Oxygen	83.6	1719					
Hydrochloric acid	190	3542	190	3500	.....	18.4	19.4
Hydrogen sulphide	213	4620	213	4580	.....	21.5	19.8
Carbon disulphide	273	6766	319	6490	6384	20.4	21.2
Carbon disulphide	318	6580					
Ether	273	7088	307	6440	6660	21.0	21.3
Ether	308	6626					
Benzene	353	7640	353	7490	7254	21.2	21.7
Propyl acetate	373	8570	375	8310	8000	22.2	21.8
Aniline	455	10740	457	10540	.....	23.1	22.6

Following Prof. Nernst's suggestion, I have examined a large number of substances in order to throw light on this relation, and if possible to derive a more accurate one. I have calculated the heat of vaporization by means of a formula devised by Nernst,[1]

$$\frac{\lambda}{1-\frac{p}{\pi}} = R\,\frac{T_1 T_2}{T_1 - T_2}\,ln\,\frac{p_1}{p_2},$$

where R is the gas constant, π the critical pressure, and p, p_1, p_2, the vapor-pressures at the temperatures T, T_1, T_2, respectively, and where T_1 and T_2 are taken near enough together so that their arithmetical and geometrical means are practically identical. As is seen in the following tables, the values thus calculated for λ' are in very satisfactory agreement with those obtained by direct observation and given under λ' obs. Only in a few cases marked with a * are the values of λ' uncertain, as shown by the irregularity of the temperature coefficients as calculated. In a few cases marked by a † it was necessary to estimate the critical pressure

[1] Loc. cit.

TABLE II.[1]

Substance.	$\frac{T_1+T_2}{2}$	$\frac{\lambda}{1-\frac{\rho}{\pi}}$	π atm.	T_o	λ' calc.	λ' obs.	$\frac{\lambda'}{T^o}$	$\frac{\lambda'}{T_o}$ obs.	8.5 log T_o.	17+0.011 T.	Diff.
Hydrogen	20.5	225.97	14.2	20.4	204	.....	10.0	.....	11.1	17.2	— 7.2
Hydrogen	20.27	221.33									
Nitrogen	75.4	144.2	27.5	77.51	1362	1334	17.6	17.2	16.1	17.8	— 0.2
Nitrogen	79.5	134.5									
*Carbon monoxide	87.3	170.3	35.5	83.0	1896	.....	18.1	.....	16.5	17.9	0.2
*Carbon monoxide	99.8	969									
Argon	86.33	1478	52.9	86.0	1460	.....	17.0	.....	16.4	18.0	— 1.0
Argon	87.02	1450									
Oxygen	89.35	1700	50.8	90.6	1664	1629	18.3	18.0	16.7	18.0	0.3
Oxygen	81.83	1735									
Methane	107.6	1994	55.2	108.3	1951	.....	18.0	.....	17.3	18.2	— 0.2
Methane	114.7	1959.6									
Krypton	121.6	2315	54.3	121.3	2270	.....	18.7	.....	17.7	18.3	0.4
Krypton	113	3085									
Xenon	163.9	3020	57.2	163.9	2970	.....	18.1	.....	18.8	18.8	— 0.7
*Hydrochloric acid	190	3542	86.0	190	3500	.....	18.4	.....	19.4	19.1	— 0.7
*Hydrogen sulphide	213	4620	92.0	213	4580	.....	21.5	.....	19.8	19.3	2.2
*Hydrogen selenide	231	4608	91.0	231	4562	.....	19.8	.....	20.1	19.5	0.3
						$T_1 = 284$					
*Ammonia	236	3923	107.6	236	3960	4950	17.0	17.4	20.2	19.6	— 2.6
*Propane	241	3514	44	236	4000	.....	17.0	.....	20.2	19.6	— 2.6
*Propane	261	4043									
Ether	308	6643	35.61	307	6466	6660	21.1	21.7	21.2	20.4	0.7
Ether	297	6744									

TABLE II—*Continued.*

Substance.	$\frac{T_1+T_2}{2}$	$\frac{\lambda}{1-\frac{\rho}{\pi}}$	π atm.	T_0.	λ' calc.	λ' obs.	$\frac{\lambda'}{T_0}$	$\frac{\lambda'}{T_0}$ obs.	8.5 log T_0.	17+0.011 T.	Diff.
Pentane	308	6739	33.03	309.5	6469	.....	20.9	.....	21.2	20.4	0.5
Pentane	298	6612									
Carbon disulphide	318	6598	77.8	319	6490	6384	20.4	20.0	21.3	20.5	— 0.1
Carbon disulphide	328	6561									
Acetone	338	6836	60.0	329.5	6850	7266	20.8	22.0	21.4	20.6	0.2
Acetone	328	6988									
Diisopropyl	318	7067	30.72	331	6627	.....	20.0	.....	21.4	20.6	—0.6
Diisopropyl	328	6895									
Chloroform	333	7351	54.9	334	7177	6984	21.5	20.9	21.5	20.7	0.8
Chloroform	338	7147									
Hexane	343	7358	29.62	342	7140	6838	20.9	20.0	21.5	20.8	0.1
Hexane	338	7486									
Carbon tetrachloride	338	7458	44.97	349.7	7190	7130	20.6	20.4	21.6	20.8	— 0.2
Carbon tetrachloride	348	7368									
Benzene	353	7665	47.89	353.4	7497	7254	21.2	20.5	21.7	20.9	0.3
Benzene	363	7410									
Hexamethylene	348	7600	39.82	353.7	7314	7342	20.7	20.8	21.7	20.9	— 0.2
Hexamethylene	358	7429									
Phenyl fluoride	353	7974	44.62	358.3	7548	.....	21.1	.....	21.7	20.9	0.2
Phenyl fluoride	363	7838									
Heptane	368	8099	26.86	371	7720	7407	20.8	20.0	21.8	21.1	— 0.3
Heptane	373	7965									
Diisobutyl	378	8380	24.55	381.5	7962	.....	20.9	.....	21.9	21.2	— 0.3
Diisobutyl	388	8149									

TABLE II—*Continued.*

Substance.	$\frac{T_1+T_2}{2}$	$\frac{\lambda}{1-\frac{p}{\pi}}$	π atm.	T_o.	λ' calc.	λ' obs.	$\frac{\lambda'}{T_o}$	$\frac{\lambda'}{T_o}$ obs.	$8.5 \log T_o$.	$17+0.011\,T_o$.	Diff.
Diisobutyl	388	8749									
Toluene	367.5	8826	41.6	383.8	8155	7695	21.3	20.0	22.0	21.2	0.1
Toluene	377.9	8355									
Stannic chloride	376.6	8540	36.95	386.9	8221	7962	21.2	20.6	22.0	21.3	— 0.1
Stannic chloride	392.2	8403									
Octane	398	8964	24.70	398	8594	8091	21.6	20.3	22.1	21.4	0.2
Phenyl chloride	408	8592									
Phenyl chloride	398	8875	44.62	405	8482	.....	20.9	.....	22.1	21.5	— 0.6
Phenyl bromide	423	9367									
Phenyl bromide	433	9293	44.62	428	9121	.....	21.3	.....	22.4	21.7	— 0.4
Dimethylorthotoluidine	454	10470	30.8	454	10130	9490	22.1	20.7	22.6	22.0	0.1
Aniline	439.5	11330									
Aniline	450.9	10900	52.35	457	10500	.....	23.0	.....	22.6	22.0	1.0
Phenyl iodide	398	10682									
Phenyl iodide	458	10054	42.62	461.4	9726	.....	20.2	.....	22.6	22.1	—1.9
Diethylaniline	483.8	11590									
Diethylaniline	471.7	12384	†31.0	488.5	10900	.....	22.2	.....	22.9	22.4	— 0.2
Chloraniline	490	12175									
Chloraniline	496.7	12220	†27.0	501.5	11700	.....	23.3	.....	23.0	22.5	0.8
p-Nitrotoluene	491.5	12150									
p-Nitrotoluene	504.2	12680	†26.6	510.7	11500	.....	22.6	.....	23.0	22.6	0.0
Chlornaphthalene	518.6	11940									
Chlornaphthalene	522.9	12120	†30.2	532.3	11600	.....	21.8	.....	23.0	22.8	— 1.0
Bromnaphthalene	548.4	12520									
Bromnaphthalene	544.5	12600	†28.9	554.1	12000	.....	21.6	.....	23.3	23.1	— 1.5

TABLE III.

Substance	$\frac{T_1+T_2}{2}$	$\frac{\lambda}{1-\frac{p}{\pi}}$	π atm.	T_o.	λ' calc.	λ' obs.	$\frac{\lambda'}{T_o}$	$\frac{\lambda'}{T_o}$ obs.	8.5 log T_o.	$17+0.011\,T_o$.	Diff.
Methyl formate.....	298	6999	56.62	305	6924	6960	22.7	22.8	21.1	20.4	2.3
Methyl formate.....	308	7061									
Ethyl formate.....	328	7396	46.83	327.2	7244	7407	22.1	22.6	21.4	20.6	1.5
Ethyl formate.....	338	7317									
Methyl acetate.....	328	7564	46.29	328	7400	8166	22.6	24.9	21.4	20.6	2.0
Ethyl acetate.....	348	8047	37.94	350	7784	7785	22.2	22.2	21.6	20.8	1.4
Ethyl acetate.....	358	7787									
Propyl formate.....	348	8143	40.05	354.2	7821	7510	22.1	21.2	21.7	20.9	1.2
Propyl formate.....	358	7947									
Ethyl propionate.....	368	8650	33.17	371.7	8273	7872	22.3	21.2	21.8	21.1	1.2
Ethyl propionate.....	378	8325									
Propyl acetate.....	373	8570	33.17	375	8310	8000	22.2	21.3	21.8	21.1	1.1
Methyl butyrate	368	8720	34.21	375.3	8247	7887	22.0	21.0	21.9	21.1	0.9
Methyl butyrate	378	8385									
Methyl salicylate.....	482	11530	†28.2	497	11000	.....	22.2	.....	23.0	22.5	— 0.4
Methyl salicylate.....	492	11440									

TABLE IV.

Substance.	$\frac{T_1 + T_2}{2}$	$\frac{\lambda}{1 - \frac{p}{\pi}}$	π atm.	T_o.	λ' calc.	λ' obs.	$\frac{\lambda'}{T_o}$	$\frac{\lambda'}{T_o}$ obs.	8.5 log T_o.	17 + 0.011 T.	Diff.
Nitric oxide	113	3085	71.2	123.1	3412	.....	27.7	.....	17.8	18.4	9.3
Nitric oxide	127.5	3625									
Chlorine	238	5496	93.5	239.4	5402	.....	22.5	.....	20.2	19.5	3.0
Chlorine	248	5243									
Bromine	328	7450	25.0	328	7200	7292	22.0	22.2	21.4	20.6	1.4
Methyl alcohol	338	8947	78.63	339	8828	8390	26.0	24.7	21.5	20.7	5.3
Methyl alcohol	348	8896									
Ethyl alcohol	338	10400	62.76	351.4	9448	9443	26.9	26.9	21.6	20.9	6.0
Ethyl alcohol	348	9785									
Propyl alcohol	378	10170	50.16	350	10000	10000	27.0	27.0	21.8	21.1	5.9
Propyl alcohol	358	10250									
Water	373	9889	194.6	373	9839	9650	26.4	25.9	21.8	21.1	5.3
Formic acid	358	8503	37.2	373	8180	.....	21.9	.....	21.8	21.1	0.8
Formic acid	368	8398									
Isobutyl alcohol	378	10700	48.27	381	10380	10250	27.2	26.9	21.9	21.2	6.0
Isobutyl alcohol	388	10370									
Acetic acid	388	9340	57.11	391	9180	5094	23.5	12.7	22.0	21.3	2.2
Acetic acid	393	9349									
Amyl alcohol	388	11385	†139	404	11080*	.....	27.4	.....	22.1	21.5	5.9
Amyl alcohol	398	11210									
Benzoic acid	514.4	14510	†28.9	522	14000	.....	26.8	.....	23.1	22.7	4.1
Benzoic acid	510.7	14800									
Mercury	628	13800	†24.6	631	13300	13560	21.1	21.5	23.8	23.9	— 2.8
Mercury	638	13750									
Sulphur	718	16643	†19.1	728	16650	23160	22.7	39.3	24.3	25.0	— 2.3
Sulphur	728	16595									

by means of the calculated value of α' and equation (2) of the preceding paper. The error is not great as the critical pressure only enters in as part of a correction term.

It is observed that the values of "Trouton's constant," in the column $\frac{\lambda'}{T_o}$, increase quite regularly with the temperature among all of the unassociated substances, given under Table II. With the exception of hydrogen and a few other substances, for which the values are uncertain, the values of $\frac{\lambda'}{T_o}$ increase as a linear function of the temperature, and are expressed quite exactly by the equation

$$\frac{\lambda'}{T_o} = 17 + 0.011T_o .$$

The earlier expression

$$\frac{\lambda'}{T_o} = 8.5 \log T_o$$

includes hydrogen but the agreement in general is less satisfactory, as is shown by this more extended study.

The values of $\frac{\lambda'}{T_o}$ for the low boiling esters as shown in Table III are higher than we should expect, as though they were associated, while the higher boiling esters have a normal value, the value of $\frac{\lambda'}{T_o}$ for all of these esters being quite constant at 22.3.

For the associated compounds given in Table IV the values of $\frac{\lambda'}{T_o}$ are considerably larger than the normal value $17+0.011T$. Hence the difference between these two quantities gives a measure of the association. The differences, *i. e.*, the values of $\frac{\lambda'}{T_o} - (17+0.011T_o)$, are given in the last column of the tables. With the alcohols, Table IV, there is practically the same difference in the case of all of the members, indicating that they have equal association. Water, the acids and especially nitric oxide are seen to be highly associated.

CONCLUSIONS.

In this paper a large number of heats of vaporization have been calculated by means of Nernst's formula and found to be in good agreement with observed values.

It has been shown that the values of "Trouton's constant" increase quite regularly and according to the equation

$$\frac{\lambda'}{T_o} = 17 + 0.011T.$$

The divergences in the case of the associated liquids have been considered to be a measure of the association.

In connection with this paper and the preceding one, I wish to express my very sincere appreciation to Prof. W. Nernst for continued counsel and advice.

BERLIN, March, 1906.

THE FREE ENERGY OF SOME HALOGEN AND OXYGEN COMPOUNDS COMPUTED FROM THE RESULTS OF POTENTIAL MEASUREMENTS.

BY M. DE K. THOMPSON.

Received March 23, 1906.

I. INTRODUCTION.

ONE of the most important chemical problems of the present time is the determination of the free energy of formation of compounds from their constituents, for it is this quantity and not the heat evolved that is the true measure of chemical affinity. No reaction can take place of itself that is not capable of doing external work, and the maximum amount of such work which a reaction can produce at any constant temperature is called the free-energy decrease of the reacting system. Although this is a vastly more important quantity than the heat evolved by the reaction, it is one which is known in few cases, compared with those for which the heat-effect has been measured. This is partly due to the greater difficulty of determining the value of the free-energy change, and partly to the fact that its importance has not until recently been generally appreciated. Just as in thermochemical investigations, so here the most fundamental data are the (free)-energy changes attending the formation of various chemical compounds out of their elements; for from these data the free-energy change attending any reaction can be calculated by direct summation.

One method of measuring the free-energy change of a chemical reaction is to determine the conditions of its equilibrium. For a reaction of the general type $aA + bB \ldots = eE + fF \ldots$ the

work W producible by the conversion of a mols of A and b mols of B at concentrations C_A', C_B' respectively into e mols of E and f mols of F at concentrations C_E', C_F' respectively, or the free-energy decrease $-\Delta F$ attending it, is given by the equation:

$$W=-\Delta F=RT\left[\log_e K-\log_e \frac{C'^e_E C'^f_F \ldots\ldots}{C'^a_A C'^b_B \ldots\ldots}+(e+f\ldots-a-b\ldots)\right]$$

in which K is the equilibrium-constant defined by the equation $K=\frac{C^e_E C^f_F \ldots}{C^a_A C^b_B \ldots}$ where C_A, C_B, $\ldots\ldots C_E$, C_F are any concentrations at which equilibrium prevails. In numerous cases, however, it is impossible to determine the equilibrium constant and therefore it is fortunate that another method is applicable to many reactions—one based on electrical potential measurements.

If the saturated solution of a salt in contact with the salt in the solid phase be electrolyzed at constant temperature between electrodes consisting of the products of decomposition, and if the process be reversible, the work done is that necessary to decompose the solid salt.[1] Conversely, the energy obtainable from this combination when working reversibly as a voltaic cell is the free energy of formation of the solid compound from its constituents. What the solvent is makes no difference in either case, provided it is not decomposed by the electrodes themselves. The solvent might be pure water, or a solution of some other salt in water, or any other liquid, so long as it is saturated with the salt in question. To take a concrete example, the free-energy change attending the formation of silver chloride could be determined either by measuring the decomposition potential between platinum electrodes of a saturated solution of silver chloride in water, or by measuring the potential of the cell: Ag | saturated solution of AgCl | Cl_2. If the cell is reversible, the two results should be identical. The latter is much the more accurate of the two methods, on account of the arbitrariness that generally accompanies the determination of decomposition points.

The free-energy decrease in any such case attending the formation of one formula weight of the solid salt out of its elements is simply the product $\nu E F$, where ν is the number of equivalent weights in one formula weight, E is the electromotive force of the combination and F the quantity of electricity whose passage

[1] Bodländer: Z. physik. Chem. 27, 55 (1898).

by Faraday's Law always attends a reaction involving one equivalent. If E is expressed in volts and F in coulombs the free energy will of course be in joules. The negative value of this product may be called simply the free energy F of the salt, that of the elements being taken as zero; and we may write therefore: $F=-\nu EF$. In case, however, one or more of the elementary substances or the compound is gaseous and ΔN mols of the gas are produced in the formation of one formula weight of the substance the free-energy equation becomes: $F=-(\nu EF+\Delta NRT)$.

The electromotive force of the above-mentioned type of cell is, however, made up of the electromotive forces at the two electrodes. Now, in many cases these separate values involved have been measured against some standard electrode for one purpose or another, and are found scattered through the literature. It is the aim of this article to summarize these results; to unite them, making a suitable correction for the potential-difference of the liquid-liquid couple, so as to give the electromotive force of a cell composed of the elementary electrodes and a saturated solution of the salt in question; and to calculate therefrom, as just described, the free energy of the salt itself.

The available data relate mainly to difficultly soluble salts; for the potential-differences of *saturated* solutions against electrodes have as a rule been measured only in the case of such salts. The necessary data also exist for a few gaseous or volatile hydrogen compounds (hydrochloric and hydrobromic acids, water, and ammonia); and computations have therefore also been made for these substances.

2. PLAN OF COMPUTATION AND PRESENTATION OF THE RESULTS.

Throughout this article the combination of an electrode with a solution will be designated a (metal-liquid) couple; the combination of two such couples a (voltaic) cell.

In evaluating the potential-differences of separate couples, the normal "calomel electrode" has always been assumed to have the value —560 millivolts at room temperature.[1] The value assigned to this has no effect, however, upon the final

[1] Ostwald: Lehrb. allgemeinen Chem., 2te Aufl. 2, 1, 944. At 25° the value is —564 millivolts. See Ostwald-Luther: Physiko-Chemische Messungen, p. 383.

results of this article, for it is eliminated in computing the electromotive force of the kind of cell in question.

No attempt has been made to reduce measurements to uniform temperature, for the necessary data are lacking, the temperature itself sometimes not being stated. As all the measurements have probably been (even in cases where the temperature is not given) made between 15° and 25°, no important error will be made in assuming that the final results apply at a temperature of 18°. The results of different observers vary much more among themselves than the error which might be involved in this assumption.

When the electromotive force is directed from the electrode to the solution, it will be considered positive; in the opposite case, negative. The electromotive force of any cell in the direction through it from left to right as it is written will therefore be the algebraic difference obtained by subtracting from the potential-difference of the first, that of the second couple. These will always be expressed in millivolts, unless otherwise stated.

In the calculation of the free energy it is assumed that one faraday F is equal to 96,600 coulombs[1] and that one joule is equal to 4.184 calories at 18°.[2] The value of the gas-constant R is taken as 8.31 joules per degree or 1.986 calories per degree.[3]

The method of working up the data may best be explained with the help of a concrete example. Let us consider the computation of the free energy of silver chloride. A table was made of the values of all the couples of the type Ag/solid AgCl+solvent, that could be found. They were of course measured against some other couple whose value is known. Very often this other couple was the "normal electrode," but not always. Then the values of all the chlorine couples were tabulated. These were of the type $Pt+Cl_2/Cl_2+$solvent, with the gaseous chlorine at atmospheric pressure. The couples which had the same solvent were then paired by taking the algebraic difference of their separate potentials, and the electromotive forces of the

[1] The recent work of Richards and Heimrod (Proc. Am. Acad. 37, 415 (1902)) has led to the value 96,580, and that of Guthe (Bull. Bureau of Standards, 1, 362 (1905)) to 96,560, which are practically identical with the round value given above.

[2] Noyes: Gen. Prin. Phys. Sci., p. 75 (1902).

[3] Ibid. p. 96.

cells of the type $Ag/AgCl+solvent/solvent+Cl_2/Pt+Cl_2$ obtained. In case the same couple had been measured by different observers, the values were first averaged before combining with that for the opposite couple.

The best method of presenting the results seems to be to tabulate first only those couples which had to be used in computing the free energy of more than one compound. These are the couples composed of various solutions and of the halogens or hydrogen or oxygen as the electrode. The other couples are used only once, and will be given where they are needed.

In gathering these data the author of this paper has consulted the following files of periodicals: *Jrb. Elektrochem.* Vols. 1-10, 1894-1903 (theoretical part of each volume examined page by page); *Z. Elektrochem.*, Vols. 1-10, 1894-1904; *Z. physik. Chem.*, Vols. 1-52, 1887-1905; *Wied. Beiblätter*, Vols. 8-28, 1884-1904; *Z. anorg. Chem.*, Vols. 1-10, 1892-1895; *J. Physic. Chem.*, Vols. 1-9, 1896-1905. In all these files except the first the indexes or the titles of all the separate articles were examined.

Table I contains the sources from which the data used in the subsequent calculations were obtained. The page numbers refer to the beginning of the article in each case. For the sake of brevity, when a reference is cited subsequently, it will be by the name of the author, and the exact page or table in which the data referred to are found will be added.

TABLE I.—LITERATURE ON THE ELECTROMOTIVE FORCE OF COUPLES CONSISTING OF ELEMENTARY ELECTRODES AND SATURATED SOLUTIONS.

Author.	Reference.
Abegg and Cox,	Z. physik. Chem. 46, 1 (1903).
Behrend,	Ibid. 11, 466 (1893); 15, 498 (1894).
Bodländer and Storbeck,	Z. anorg. Chem. 31, 1, 458 (1902).
Boericke,	Z. Elektrochem. 11, 57 (1905).
Brönsted,	Z. physik. Chem. 50, 481 (1904).
Calame,	Ibid. 27, 401 (1898).
Carveth,	J. Physic. Chem. 2, 298 (1898).
Danneel,	Z. physik. Chem. 33, 415 (1900).
Dolezalek,	Ibid. 26, 321 (1898).
Findlay,	Ibid. 30, 628 (1899).
Goodwin,	Ibid. 13, 577 (1894).
Immerwahr,	Z. Elektrochem. 7, 477 (1900).
Küster and Crotogino,	Z. anorg. Chem. 23, 87 (1900).
Küster and Thiel,	Ibid. 23, 25 (1900).
Lovén,	Z. physik. Chem. 20, 456 (1896).
Luther,	Ibid. 30, 628 (1899); 36, 385 (1901).

Author.	Reference.
Luther and Wilson,	Ibid. 34, 488 (1900).
McIntosh,	J. Physic. Chem. 27, 417 (1898).
Müller,	Z. physik. Chem. 40, 158 (1902).
Neumann,	Ibid. 14, 193 (1894).
Rothmund,	Ibid. 31, 69 (1899).
Sammet,	Ibid. 53, 641 (1905).
Sauer,	Ibid. 47, 146 (1904).
Smale,	Ibid. 14, 577 (1894); 16, 562 (1895).
Thiel,	Z. anorg. Chem. 24, 1 (1900).
Wilsmore,	Z. physik. Chem. 35, 291 (1900).
Zengelis,	Ibid. 12, 298 (1893).

3. LIQUID-LIQUID COUPLES INVOLVED IN SUBSEQUENT COMPUTATIONS.

The electromotive forces of the liquid-liquid couples that are involved in the subsequent computations may next be tabulated. Some of these have been computed by me for a temperature of 17° by the formula derived by Planck,[1] and some were found in the literature, as is shown by the foot-notes. The couples are so written that the direction of the electromotive force is from left to right. The letter N preceding a chemical symbol is used throughout this article to represent a concentration of one equivalent (in grams) per liter of solution.

TABLE II.—THE ELECTROMOTIVE FORCE OF CERTAIN LIQUID-LIQUID COUPLES.

Couple.	E.m.f. in millivolts.	Couple.	E.m.f. in millivolts.
N/10 KCl | N/10 NaOH	21	N/10 KNO_3 | N/10 KOH	17
N/10 KCl | N/10 $Ba(OH)_2$	21	N/1 KCl | N/10 KOH	5
N/10 KCl | N/10 KOH	16	N/100 HCl | N/1 KCl	7
N/10 HBr | N/1 KCl	14	N/10 HCl | N/10 KCl[2]	28
N/10 NaCl | N/10 NaOH	18	N/10 HCl | N/10 NaCl[2]	33
N/10 KNO_3 | N/10 KCl	1	N/10 KCl | N/10 NaCl[2]	5
N/10 KNO_3 | N/10 $AgNO_3$	3	N/1 KCl | N/1 NaOH[3]	21
N/10 KNO_3 | N/1 KCl	1	N/10 HCl | N/100 HCl[4]	38
N/1 KCl | N/20 NaOH	3	N/100 HCl | N/10 KCl[4]	24
N/20 NaCl | N/1 KCl	2	N/10 KCl | N/1 KCl[5]	0.3
N/1 KCl | N/10 $Ba(OH)_2$	6	N/1 HCl | N/1 KCl[5]	28
N/10 KNO_3 | N/10 NaOH	23	N/1 HCl | N/10 HCl[5]	36

[1] Wied. Ann. 40, 561 (1890).

[2] Negbauer: Weid. Ann. 44, 737 (1891), Table 14.

[3] Smale, p. 611. [4] Wilsmore, p. 303. [5] Sauer.

4. COUPLES INVOLVING HALOGEN OR OXYGEN ELECTRODES.

As stated above, all of the couples involving halogen or oxygen electrodes needed in these calculations were not measured in combination with the "normal electrode." Some of them are derived from cells, the other electrode of which is hydrogen. The electromotive force data for the hydrogen electrode against solutions of various hydrogen-ion concentration have been critically considered by Wilsmore;[1] and his final values have therefore been adopted in these calculations. That for the hydrogen electrode against a normal hydrogen-ion solution is —277 millivolts; and those against various hydrochloric acid solutions, obtained in part by graphic interpolation, are as follows:

Solution.	Concentration.	E.m.f. × (—1).
HCl	N/1	271
"	N/10	217
"	N/20	200
"	N/100	161

The electromotive forces of the couples involving halogen or oxygen electrodes are given in millivolts in Tables III to VI. The values are the so-called absolute potentials, taking the value of the "calomel electrode" as —560 millivolts. A positive sign of the electromotive force of the electrode couple shows that the force acts in the direction from the electrode to the solution; a negative sign that it acts in the opposite direction. In the case of the liquid-liquid couples the value is written in the table with a negative sign when the direction of the electromotive force coincides with that of the cell, as in that case it has to be subtracted. When acting in the opposite direction, it is written with the positive sign. The chlorine and oxygen electrodes were saturated with these gases at atmospheric pressure; those of bromine or iodine, with these elements at the concentrations of their saturated solutions. The abbreviation N. E. is used to represent the so-called "normal electrode," N/1KCl, HgCl/Hg.

[1] Z. physik. Chem. 35, 302; 36, 92 (1900).

TABLE III.—COUPLES INVOLVING THE CHLORINE ELECTRODE ($Pt+Cl_2$)

Temp.	Solution.	E.m.f. of chlorine couple ×(−1).	Cell measured.	E.m.f. of cell.	E.m.f. of other couple ×(−1).	E.m.f. of liquid-liquid couple.	Reference to cell measurement.
17°	N/1 HCl	1612[1]	H_2 | N/1 HCl | Cl_2	1341	271	0	Smale: Z. physik. Chem. 16, 563.
18°	N/1 HCl	1639	H_2 | N/1 HCl | Cl_2	1368	271	0	McIntosh, p. 285.
25°	N/1 HCl	1637	H_2 | N/1 HCl | Cl_2	1366	271	0	Müller.
18°	N/1 HCl	1652	N.E. | N/1 HCl | Cl_2	1064	560	+28	McIntosh, p 285.
Mean		1643					
18°	N/10 HCl	1703	H_2 | N/10 HCl | Cl_2	1486	217	0	McIntosh.
25°	N/10 HCl	1702	H_2 | N/10 HCl | Cl_2	1485	217	0	Müller.
18°	N/10 HCl	1712	N.E. | N/10 HCl | Cl_2	1138	560	+14	McIntosh, p. 285.
18°	N/10 HCl	1710	Cl_2 | N/1 HCl | N/10 HCl | Cl_2	103	1643	—36	Ibid., Table 8.
Mean		1707					
18°	N/100 HCl	1716	H_2 | N/100 HCl | Cl_2	1555	161	0	McIntosh.
25°	N/100 HCl	1707	H_2 | N/100 HCl | Cl_2	1546	161	0	Müller.
18°	N/100 HCl	1727	N.E. | N/100 HCl | Cl_2	1160	560	+ 7	McIntosh, p. 285.
..	N/100 HCl	1710	Cl_2 | N/10 HCl | N/100 HCl | Cl_2	41	1707	—38	Ibid., Table 8.
Mean		1715					
17°	N/1 KCl	1617	N.E. | N/1 KCl | Cl_2	1057	560	0	Smale, Table 5.
..	N/5 KCl	1666	.....	....	...	..	Neumann.
17°	N/1 NaCl	1603	N.E. | N/1 NaCl | Cl_2	1048	560	—5	Smale, Table 5.

[1] Omitted in taking the mean.

The following table contains the means of the measurements made on the same couple.

TABLE IV.—FINAL VALUES OF COUPLES INVOLVING THE CHLORINE ELECTRODE ($Pt+Cl_2$) AT 18°.

No.	Solution.	E.m.f. × (−1).	No.	Solution.	E.m.f. × (−1).
1	N/1 HCl	1643	6	N/1 KCl	1617
2	N/10 HCl	1707	7	N/2 KCl[1]	1636
3	N/20 HCl[1]	1709	8	N/5 KCl	1666
4	N/50 HCl[1]	1713	9	N/10 KCl[2]	1703
5	N/100 HCl	1715	10	N/1 NaCl	1603

It will be noticed that these potentials do not change with the concentration in accordance with the theory, from which the desirability of new measurements of the chlorine electrode in solutions of different chlorine-ion concentrations is evident. The deviations could of course be equalized upon a theoretical basis, but it is deemed best to base all these computations upon empirical data. It is probable that it is only the values for the 0.01 normal and the 0.02 normal hydrochloric acid that are seriously in error.[3]

[1] Interpolated graphically.

[2] Extrapolated graphically.

[3] It is a well-known fact that when chlorine is dissolved in water, it does not all remain in the form of molecular chlorine. Owing to the occurrence of the reaction,

$$Cl_2+H_2O=HOCl+H^++Cl^-,$$

the concentration of the chlorine ions is increased to a certain extent (Jakowkin: Z. physik. Chem. 29, 613 (1899)). It takes several hours, however, for this equilibrium to be established (Ibid., p. 625), and it is, therefore, doubtful whether, in measuring chlorine electrodes, the solution surrounding the electrode is allowed to stand in contact with the chlorine gas long enough to reach this state. Even granting that equilibrium is established, the following considerations will show that the effect on the potential for all couples used below would never exceed 7 millivolts. The solubility of chlorine in pure water is 0.089 mol. per liter (see Landolt-Börnstein-Meyerhoffer's tables, 3rd edition, p. 601, under column 1), of which 0.025 mol. is hydrolyzed (Boericke: Loc. cit., p. 63). According to the mass action law,

$$C_H \times C_{Cl} \times C_{HClO}=\text{const.} \times C_{Cl_2}.$$

But in saturated solutions, C_{Cl_2} is constant, and therefore

$$C_H \times C_{Cl} \times C_{HClO}=\text{const.}=(0.025)^3.$$

If the original concentration of hydrochloric acid is C_A, the new amount C of hydrochloric acid produced upon saturating the solution with chlorine is given by the equation

$$C(C_A+C)^2=(0.025)^3.$$

Before giving the values of the couples involving the bromine electrode, a few prefatory remarks are necessary. When bromine is dissolved in a solution of hydrobromic acid or of a bromide, it adds itself to the bromide to form tribromide, in case only small quantities of bromine are added, while higher bromides are formed if the solution is saturated with bromine.[1] It is evident, therefore, that if we start with a normal solution of potassium bromide and saturate it with bromine, the solution no longer contains the usual quantity of bromide ions. There are in solution unknown amounts of KBr, KBr_3, KBr_5 and possibly higher bromides. Only the ions of the first of these compounds affect the electromotive force. Thus in combining with a bromine couple, a couple consisting of a silver electrode dipping in a normal solution of potassium bromide saturated with silver bromide, the former couple should theoretically consist of a bromine electrode in contact with a solution saturated with bromine and containing as many bromide ions per liter as the silver couple. In order to obtain such a bromine couple, a considerably stronger solution of potassium bromide would have to be started with. Measurements with such cells do not exist, but the electromotive forces of bromine electrodes dipping into solutions saturated with bromine and containing known amounts of bromide ions may be computed as follows. Let K be the equilibrium ratio for the reaction $Br_2 = 2Br^- + 2F^+$, defined by the equation $K = \frac{(C_{Br^-})_0^2}{(C_{Br_2})_0}$ and let (C_{Br^-}) and (C_{Br_2}) be the concentrations of bromide ions and free bromine molecules in any solution. The electromotive force of a bromine electrode against such a solution is then given by the formula

$$E = \frac{RT}{2F}\left[\log K - \log \frac{(C_{Br^-})^2}{C_{Br_2}}\right] = E_0 - \frac{RT}{2F}\log\left[\frac{(C_{Br^-})^2}{C_{Br_2}},\right]$$

When C_A is 0.1, C is 0.001, which is negligible. For 0.01 normal solution the correction amounts to 7 millivolts, but for the reason stated above, it is deemed best to leave this correction out of consideration.

In hydrochloric acid solutions a certain amount of HCl_3 is formed, which at 0° and in a 0.2 normal solution amounts to 0.8 per cent. (Jakowkin: *loc. cit.*, p. 635). The amount which would be formed at 17° is not known, but it could not introduce a serious error.

[1] Jakowkin: Z. physik. Chem. 20, 19 (1896).

[2] It may be well here to call attention to the fact that the C's are customarily given in mols. per liter.

where E_0, the so-called electrolytic potential, is the value of E when C_{Br^-} and C_{Br_2} are both unity. From measurements in solutions where the concentrations C_{Br^-} and C_{Br_2} could be computed the value of E_0 has been derived by two different observers,[1] the mean of whose values is $E_0 = -1.373$ volts at 25°. From this value, by means of the above formula, may be computed the potential of a bromine electrode dipping in a solution with any desired concentration of bromine molecules and bromide ions. A little consideration will show that the concentration of the bromine molecules here needed is substantially that of a saturated solution in pure water and that the concentration of the bromide ions involved is that which exists in water solutions of the bromide. In computing the following tables, the solubility of bromine in water at 25° is taken as 0.2125 mol per liter.[2] The potentials are computed for the electrode dipping in potassium bromide and also in hydrobromic acid, since the difference in dissociation between the salt and the acid causes a small variation in the potential.

TABLE V.—COUPLES INVOLVING THE BROMINE ELECTRODE ($Pt + Br_2$) at 25°.

Solution.	E.m.f. × (−1).	Solution.	E.m.f. × (−1).
N/1 KBr	1361	N/1 HBr	1359
N/2 KBr	1377	N/2 HBr	1375
N/5 KBr	1399	N/5 HBr	1397
N/10 KBr	1416	N/10 HBr	1414
N/20 KBr	1433	N/20 HBr	1431

In the case of the iodine electrode, considerations similar to those mentioned in the case of the bromine electrode apply. Here, however, the computation of the iodide ion concentrations is much simpler, as the ratio $\frac{KI_3}{KI + KI_3}$ for saturated solutions of iodine in potassium iodide has been found by Noyes and Seidensticker[3] to be almost exactly 0.5. From this datum Sammet[4] has computed the concentrations of the iodide ions in the solutions used by Crotogino, and has also duplicated his potential measurements. The maximum variation in these two sets of measure-

[1] Boericke: Loc. cit., p. 71, found −1.375 volts; Sammet: Z. physik. Chem. 53, 681 (1905), found −1.371 volts.

[2] Boericke: Loc. cit.

[3] Z. physik. Chem. 27, 357 (1898).

[4] Loc. cit., Table 25.

ments is 1 millivolt. Plotting the logarithms of these iodide ion concentrations against the corresponding electromotive forces, a straight line is obtained from which may be read off the electromotive forces of iodine electrodes dipping into potassium iodide solutions saturated with iodine and containing the desired quantity of iodide ions. Table VI contains the results of this computation. The first and third columns give the strength of the solution which would have the stated voltage, if the iodine did not combine with the iodide. The actual solution is about twice as strong.

TABLE VI.—COUPLES INVOLVING THE IODINE ELECTRODE (Pt.$+I_2$) at 25°.

Solution.	E.m.f $\times$ (−1).	Solution.	E.m.f. $\times$ (−1).
N/1 KI	824	N/10 KI	883
N/2 KI	842	N/20 KI	901
N/5 KI	865		

There have been no measurements of the iodine electrode in solutions of hydriodic acid saturated with iodine. These values, however, would (as in the case of the bromine compounds) not be much different from the above. The only cause for difference would be in the unequal degree of dissociation of the salt and the acid.

For the potential of the oxygen electrode as derived from measurements of the hydrogen-oxygen cell, various values have been obtained. Thus for the electromotive force of that cell Smale first found about 1.08, Wilsmore[1] later 1.12, and Bose[2] very recently 1.14; and it has been clearly shown that the variation arises on the side of the oxygen, not the hydrogen electrode. In view of this uncertainty it has seemed best to adopt for the cell the value 1.22, which has just been derived independently through the study of chemical equilibria at high temperatures by three different investigators.[3]

The following table contains in the second column the values of the oxygen-liquid couples needed in these computations. The following columns give the data from which these are computed. The values of the electromotive force of the "cell measured" are taken from Smale's paper. By subtracting from this the electromotive force of the normal electrode (560 milli-

[1] Loc. cit., p. 298.

[2] Z. physik. Chem. 38, 1 (1901).

[3] Lewis: This Journal, 28, 158 (1906); Haber: Z. Electrochem. 11, 834; Nernst: Ibid., 835.

volts) and adding that of the liquid-liquid couple, that of the hydrogen couple involved in the cell is obtained; and by subtracting this from 1220 that of the corresponding oxygen electrode results.

TABLE VII.—COUPLES INVOLVING THE OXYGEN ELECTRODE ($Pt + O_2$) at 17°.

Solution.	E.m.f. of couple × (—1).	Cell measured.	E.m.f. of of cell.	E.m.f. of liquid-liquid couple.	E.m.f. of hydrogen couple.
N/1 NaOH	710	H_2 | N/1 NaOH | N.E.	1052	+21	513
N/KOH	710	H_2 | N/1 KOH | N.E	1053	+16	509
Mean	710				
N/10 NaOH	760	H_2 | N/10 NaOH | N.E.	1015	+ 6	461
N/10 KOH	750	H_2 | N/10 KOH | N.E	1027	+ 5	472
Mean	755				
N/20 KOH or NaOH	768[1]				

5. ELECTROMOTIVE FORCE OF CELLS CONSISTING OF SATURATED SOLUTIONS OF CERTAIN HALIDES AND OXIDES AND ELECTRODES OF THEIR CONSTITUENTS.

The following series of tables shows the directly measured electromotive force of cells consisting in part of a metallic electrode and a saturated solution of one of its salts; the electromotive force of this electrode-liquid couple (called below the "first couple") together with the data involved in its derivation—the electromotive force of the other ("second") electrode-liquid couple and that of the liquid-liquid junction; and finally the electromotive force of a cell composed of the metallic electrode (M), the saturated solution of the salt (MA) and the non-metallic electrode (A), calculated by taking the algebraic difference between the electromotive force of the electrode-liquid couple just referred to, and that of the appropriate couple (with the same readily soluble electrolyte) given in Section 4. The first cell here referred to will be called the "measured cell" ("M. C.") and the second cell the "derived cell" ("D. C."). The cells are always written so that the direction of the current through the cell is from left to right.

The final mean value for each cell is obtained by averaging the values in the last column of each table, weights being assigned to each mean value equal to the number of measurements of the metallic couple. To change from volts to small calories, where one equivalent is involved, the factor $23{,}090 = \frac{96{,}600}{4.18}$ is employed.

[1] Extrapolated graphically.

TABLE VIII.—SILVER | SILVER CHLORIDE | CHLORINE.

Authority.	Cell measured = M. C.	Temp.	M. C.	Electromotive force of: Second couple, M. C.	Liquid-liquid couple.	First couple, M. C. and D. C.	Second couple, D. C.	D. C.
Küster and Thiel	Ag | AgCl, N/1 KCl | N.E	25°	50	— 564	..	—514	—1617	1103
Luther, p. 648	Ag | AgCl, N/10 HCl | N/10 HCl, HgCl | Hg	..	..	....	..	—554	—1707	1153
Zengelis	Ag | AgCl, N/1 NaCl | N.E.	..	35	— 560	+5	—520	—1603	1083
Zengelis	Ag | AgCl, N/10 KCl | N/10 KNO_3 | N/10 $AgNO_3$ | Ag	..	460	—1016[1]	—2	—558		
Goodwin, Table 27	Ag | AgCl, N/10 KCl | N/10 KNO_3 | N/10 $AgNO_3$ | Ag	25°	450	—1016	—2	—568		
Brönsted	Ag | AgCl, N/10 KCl | N/10 KCl, HgCl | Hg	15°	43.7	— 614	..	—570		
Lovén	Ag | AgCl, N/10 KCl | N/10 KNO_3 | N/10 $AgNO_3$ | Ag	15°	443.3	—1016	—2	—575		
Abegg and Cox	N.E. | N/10 KCl, AgCl | Ag	25°	15	—564	..	—579		
						Mean = —570	—1703	1133
							Final mean,	1123

Free energy of AgCl: —25,600 cal.

[1] Zengelis: Loc. cit. This value is derived from the e.m.f. of the cell N.E. | N/10 KNO_3 | N/10 $AgNO_3$ | Ag which is 0.458 volt or 0.456 corrected for junctions.

TABLE IX.—SILVER | SILVER BROMIDE | BROMINE.

Authority.	Cell measured.	Temp.	Electromotive force of: M. C.	Second couple, M. C.	Liquid-liquid couple.	First couple, C. and D	M. C.	Second couple, D. C.	D. C.
Küster and Thiel	Ag | AgBr, N/1 KBr | N.E.	25°	198	— 564	..	—366	—1361		995
Zengelis	Ag | AgBr, N/10 KBr | N/10 KNO_3 | N/10 $AgNO_3$ | Ag	..	600	—1016	—2	—418			
Abegg and Cox	Ag | AgBr, N/10 KBr | N.E.	25°	133	— 564	..	—431			
Lovén	Ag | AgBr, N/10 KBr | N/10 KNO_3 | N/10 $AgNO_3$ | Ag	16°	601	—1016	—2	—417			
Goodwin	Ag | AgBr, N/10 KBr | N/10 KNO_3 | N/10 $AgNO_3$ | Ag	25°	599	— 101	—2	—419			
						Mean,	—421	—1416	995
Luther, p. 648	Ag | AgBr, N/10 HBr | N/10 HCl, HgCl | Hg	..	...	....	..	—405	—1414		1009
								Final mean,	997

Free energy of AgBr: — 23,000 cal.

TABLE X.—SILVER | SILVER IODIDE | IODINE.

Authority.	Cell measured.	Temp.	Electromotive force of					
			M. C.	Second couple, M. C.	Liquid-liquid couple,	First couple, M. C. and D. C.	Second couple, D. C.	D. C
Thiel	Ag | AgI, N/1 KI | N.E.	25°	422.8	—564	...	—141	—824	683
Zengelis	Ag | AgI, N/10 KI | N/10 KNO_3 | N/10 $AgNO_3$ | Ag	..	836	—1016	—2	—182		
Lovén	Ag | AgI, N/10 KI | N/10 KNO_3 | N/10 $AgNO_3$ | Ag	14.5°	816.5	—1016	—2	—202		
Goodwin	Ag | AgI, N/10 KI | N/10 KNO_3 | N/10 $AgNO_3$ | Ag	25°	814	—1016	—2	—204		
					Mean,	—196	—883	687
Danneel	Ag | AgI, N/10 HI | N/10 HI | H_2	..	23[1]	—217	0	—194	—883	689
							Final mean,	687

Free energy of AgI: —15,900 cal.

[1] Interpolated graphically.

TABLE XI.—MERCURY | MERCUROUS CHLORIDE | CHLORINE.

Authority.	Cell measured.	Temp.	Electromotive force of: M. C.	Second couple, M. C.	Liquid-liquid couple.	First couple, M. C. and D. C.	Second couple, D. C.	D. C.
Smale	N.E. | N/1 KCl | Cl_2	17°	1057	....	....	....	....	1057
Calame, p. 417	N.E | N/10 KCl, HgCl | Hg	..	56	—560	+0.3	—616.3		
Sauer	N.E. | N/10 KCl, HgCl | Hg	18°	51.4	—560	+0.3	—611.7		
						Mean, —614	—1703	1089
Sauer	Hg | HgCl, N/1 HCl | N.E.	18°	32.3	—560	—28	—556		
Carveth	D.E.[1] | N/1 HCl, HgCl | Hg	..	557	0	0	—557		
						Mean, —557	—1643	1086
Sauer	Hg | HgCl, N/10 HCl | N/10 KCl, HgCl | Hg	18°	28.6	—614	—28	—613		
Sauer	Hg | HgCl, N/1 HCl | N/10 HCl, HgCl | Hg	18°	98.8	—557	—36	—620		
Carveth	D.E. | N/10 HCl, HgCl | Hg	..	605	0	0	—605		
						Mean, —619	—1707	1088
Immerwahr	N.E. | N/1 KNO_3, N/20 KCl, HgCl | Hg	..	76.8	—560	0	—637	—1709	1072
								Final mean, 1083

Free energy: —49,400 cal.

[1] "Dropping Electrode."

TABLE XII.—MERCURY | MERCUROUS BROMIDE | BROMINE.

Authority.	Cell measured.	Temp.	Electromotive force of: M. C.	Second couple, M. C.	Liquid-liquid couple.	First couple, M. C. and D. C.	Second couple, D. C.	D. C.
Behrend	Hg | HgBr, N/10 KBr | N/10 KCl, HgCl | Hg	ab't 20°	131	—614	0	—483		
Goodwin, Table 33	Hg | HgBr, N/10 KBr | N/10 KCl, HgCl | Hg	15–18°	133.8	—614	0	—480		
					Mean,	—481	—1416	935
Immerwahr	Hg | HgBr, N/1 KNO_3 N/20 KBr | N.E.	....	39	—560	0	—521	—1433	912
							Final mean,	927

Free energy: —42,800 cal.

TABLE XIII.—MERCURY | MERCUROUS IODIDE | IODINE.

Behrend	Hg | HgI, N/10 KI | N/10 KCl, HgCl | Hg	ab't 20°	322	—614	0	—292	—883	591
Immerwahr	Hg | HgI, N/1 KNO_3, N/20 KI | N.E.	....	226.4	—560	0	—334	—901	567
							Final mean,	579

Free energy: —26,800 cal.

TABLE XIV.—COPPER | CUPROUS CHLORIDE | CHLORINE.

Authority.	Cell measured.	Temp.	Electromotive force of: M. C.	Second couple, M. C.	Liquid-liquid couple.	First couple, M. C. and D. C.	Second couple, D. C.	D. C.
Immerwahr[1]	Cu | CuCl, N/1 KNO_3, N/20 HCl | N.E.	..	95	—560	0	—465	—1709	(1244)
Luther and Wilson	Cu | CuCl, N/20 KCl | N.E.	25°	..	—564	..	—491	—1709	1218
							Final mean,	1218

Free energy: —27,800 cal.

TABLE XV.—COPPER | CUPROUS BROMIDE | BROMINE.

Immerwahr	Cu | CuBr, N/1 KNO_3, N/20 KBr | N.E.	..	156	—560	0	—404		
Luther and Wilson	Cu | CuBr, N/20 KBr | N.E.	25°	..	—564	..	—410		
Bodländer and Storbeck	Cu | CuBr, N/20 KBr | N.E.	..	..	...	..	—402		
						Final mean,	—1433	1028

Free energy: —23,700 cal.

TABLE XVI.—COPPER | CUPROUS IODIDE | IODINE.

Immerwahr	Cu | CuI, N/1 KNO_3, N/20 KI | N.E.	..	373	—560	0	—187		
Bodländer and Storbeck	Cu | CuI, N/20 KI | N/20 KBr, CuBr | Cu	..	225.8	—405	0	—179		
						Final mean,	—901	718

Free energy: —16,600 cal.

[1] Omitted. See Luther: Z. physik. Chem. 36, 385 (1901).

TABLE XVII.—THALLIUM | THALLOUS CHLORIDE | CHLORINE.

Authority.	Cell measured.	Temp.	Electromotive force of: M. C.	Second couple, M. C.	Liquid-liquid couple.	First couple, M. C. and D. C.	Second couple, D. C.	D. C.
Neumann	Tl | Tl sat. in H_2O[1] | N.E.	..	..	..	..	151	—1715	1866
Goodwin, Table 2	Tl | TlCl, N/5 KCl | N/5 KNO_3, TlCl | Tl	25°	59.0	+151	+1	211	—1666	1877
Goodwin, Table 2	Tl | TlCl N/10 KCl | N/10 KNO_3, TlCl | Tl	25°	44.2	+151	+1	196	—1703	1899
Goodwin, Table 2	Tl | TlCl N/20 KCl | N/20 KNO_3, TlCl | Tl	25°	30.1	+151	+1	182	—1709	1891
							Final mean,	1883

Free energy: —43,200 cal.

TABLE XVIII.—THALLIUM | THALLOUS BROMIDE | BROMINE.

Goodwin, Table 34	Tl | TlBr, N/5 KBr | N/5 KCl, TlCl | Tl	25	101.3	+211	0	312	—1399	1711
Goodwin, Table 34	Tl | TlBr, N/10 KBr | N/10 KCl, TlCl | Tl	25	100.7	+196	0	297	—1416	1713
Goodwin, Table 34	Tl | TlBr, N/20 KBr | N/20 KCl, TlCl | Tl	25	99.1	+182	0	281	—1433	1714
							Final mean,	1713

Free energy: —39,600 cal.

[1] Concentration of ions is 0.01 normal. See Wilsmore, Loc. cit.

TABLE XIX.—LEAD | LEAD CHLORIDE | CHLORINE.

Authority.	Cell measured.	Temp.	Electromotive force of: M. C.	Second couple, M. C.	Liquid-liquid couple.	First couple, M. C. and D. C.	Second couple, D. C.	D. C.
Neumann	Pb | $PbCl_2$ sat. in H_2O[1] | N.E.	..	..	....	..	—95	—1709	1614
Zengelis	Pb | $PbCl_2$, N/10 KCl | N.E.	..	546	—560	0	—14	—1703	1689
Immerwahr	Pb | $PbCl_2$, N/2 KCl, N/1 KNO_3 | N.E.	..	514	—560	0	—46	—1636	1590
Immerwahr	Pb | $PbCl_2$, N/20 KCl, N/1 KNO_3 | N.E.	..	482.6	—560	0	—77	—1709	1632
Immerwahr	Pb | $PbCl_2$, N/20 HCl, N/1 KNO_3 | N.E.	..	484.6	—560	0	—75	—1709	1634
							Final mean,	1632

Free energy: —74,800 cal.

TABLE XX.—LEAD | LEAD BROMIDE | BROMINE.

Zengelis	Pb | $PbBr_2$, N/10 KBr | N.E.	..	561	—560	0	1	—1416	1417
Immerwahr	Pb | $PbBr_2$, N/20 KBr, N/1 KNO_3 | N.E.	..	493.0	—560	0	—67	—1433	1366
							Final mean,	1391

Free energy: —64,200 cal.

[1] Concentration of lead ions is 0.04 N (Wilsmore, l.c.). Attention is here called to the fact that Wilsmore used the word "normal" in the sense of "molal." This makes a correction necessary for the electrolytic potentials as given by him in the case of all except univalent metals. For bivalent metals the correction amounts to 8 millivolts. This has been overlooked by ertain authors who have copied his data.

TABLE XXI.—LEAD | LEAD IODIDE | IODINE.

Authority.	Cell measured.	Temp.	Electromotive force of: M. C.	Second couple, M. C.	Liquid-liquid couple.	First couple, M. C. and D. C.	Second couple, D. C.	D. C.
Zengelis	Pb | PbI_2, N/10 KI | N.E.	..	617	—560	0	+57		
Findlay	Pb | PbI_2, N/10 NaI | N.E.	25°	(574)[1]	—564	0	+10		
						—		
						Mean, 33	—883	916
Findlay	Pb | PbI_2, N/20 NaI | N.E.	25°	(556[1])	—564	0	— 8		
Immerwahr	Pb | PbI_2, N/1 KNO_3, N/20 KI | N.E.		546.0	—560	0	—14		
						—		
						Mean, —11	—901	890
							Final mean,	903

Free energy: —41,700 cal.

[1] Not given in the original paper, but computed from the value of each couple.

TABLE XXII.—MERCURY | MERCUROUS OXIDE | OXYGEN.

Authority.	Cell measured.	Temp.	Electromotive force of: M. C.	Second couple, M. C.	Liquid-liquid couple.	First couple, M. C. and D. C.	Second couple, D. C.	D. C
Wilsmore	Hg | Hg_2O, N/1 KOH | N.E	25°	..	..	..	—415		
Smale, p. 611	Hg | Hg_2O, N/1 NaOH | N.E	17°	129.6	—560	+20.5	—410		
					Mean,	—413	—710	297
Behrend	Hg | Hg_2O, N/10 NaOH | N/10 KNO_3 | N/10 KCl, HgCl | Hg ab't	20°	130	—614	+22	—462	—760	300
Behrend	Hg | Hg_2O, N/10 KOH | N/10 KNO_3 N/10 KCl, HgCl | Hg ab't	20°	143	—614	+16	—455	—750	290
						Final mean,		296

Free energy: —13,400 cal.

TABLE XXIII.—SILVER | SILVER OXIDE | OXYGEN.

Abegg and Cox	N.E. | N/10 $Ba(OH)_2$, Ag_2O | Ag.	25°	111	—564	—6	—669	—760	91

Free energy: —3,910 cal.

In the case of chlorides of the type MCl the free energy of one molecule is calculated by the expression—(EF—0.5 RT) which is equal in calories to—(23,090E—288), while for bromides and iodides the term 0.5 RT drops out. For chlorides of the type MCl_2 the free energy of one mol. is—(2EF—RT) while in the case of bromides and iodides of this type the term RT is again omitted. For oxides of the types MO and M_2O the free energy is— (2EF—0.5 RT).

6. COMPUTATION OF THE FREE ENERGY FROM SOLUBILITY AND ELECTROLYTIC POTENTIALS.

The free energy of one mol consisting of N equivalents, of an n-ionic solid compound may also be calculated from the electrolytic potentials E_C and E_A of its elements (of which let N mols be gaseous), and from the solubility S of the compound (expressed in equivalents per liter and regarded as completely ionized) by the following formula, which in somewhat different form was first derived by Bodländer:[1]

$$-F = (E_C - E_A)NF - nRT \log S - NRT.$$

It is, therefore, of interest to compare the results obtained in this way with those computed above directly from decomposition-potentials of the saturated solutions.

For this purpose the electrolytic potentials for the metals are taken from Wilsmore's paper. With respect to the non-metals it is important to note that in the case of all elements whose concentrations in the electrode can be varied, such as the halogens

[1] Loc. cit. The above formula may also be deduced by the following reversible process in which one mol of an n-ionic salt consisting of N equivalents is formed from its elements, of which N mols may be gaseous. Make use of a cell consisting of the elementary substance as electrodes dipping into a normal solution of the corresponding ions. Let this cell act reversibly until N equivalents of the elementary substances have gone into solution as ions, at the same time adding to the solution reversibly the quantity of water necessary to keep the concentration constant. The work done by the cell in this process is $(E_C - E_A)NF - NRT + nRT$. Now allow the salt to change its concentration to that corresponding to its solubility S (by cutting off the quantity of solution which contains one mol and diluting it); assuming it is completely dissociated in both solutions, the work done by the system in this process is $nRT \log 1/S$. Now force the salt out of solution by means of a semi-permeable piston, in which the work done by the system is $-nRT$. The total work done by the system is therefore $(E_C - E_A)\,NF + nRT \log 1/S - NRT$.

and oxygen, there are two kinds of specific electrolytic potentials—one, where the solution is saturated with respect to the element in question, the other, where the solution is molal with respect to it, the solution being molal with respect to the ions of the element in both cases.[1] It is evident the former is the proper one to employ in these computations. For computing the electrolytic potential of chlorine Sullivan's[2] value of the equilibrium ratio for the reaction $Cl_2 = 2Cl^- + 2\mathfrak{F}^+$ has been adopted. The value of the solubility of chlorine in pure water is 0.089 mol per liter at 25°. It would, however, be less in a solution normal with respect to chloride ions. There is good reason for the assumption that in a normal potassium chloride solution the solubility at 25° would be only 81 per cent. of the above amount,[3] and for a solution normal with respect to chloride ions, the reduction in solubility would probably not be much greater. Therefore, the solubility is taken as 0.072 mol per liter. The resulting value of the electrolytic potential differs by 1 millivolt from the value computed by Haber.[4]

In computing the electrolytic potential of bromine with respect to a solution saturated with bromine molecules, the solubility is taken the same as in pure water, 0.2125 mol per liter at 25°. By means of this datum the electrolytic potential with respect to a solution saturated with bromine molecules is computed from the electrolytic potential used above with respect to a solution molal with bromine molecules. The electrolytic potential of iodine in a solution saturated with respect to iodine molecules may be obtained exactly as the values in Table VI, and therefore depends on Crotogino's measurements.

The following table gives the results of this computation.

TABLE XXIV.—THE ELECTROLYTIC POTENTIALS OF THE HALOGENS IN SOLUTIONS SATURATED WITH THEM AT 25°.

E_{Cl_2}	−1.643
E_{Br_2}	−1.353
E_{I_2}	−0.817

The values of the solubilities are taken from the third edition of Landolt-Börnstein-Meyerhoffer's tables, and only those are used

[1] See Haber: Z. Elektrochem. p. 1047.

[2] Z. physik. Chem. **28**, 523 (1899), $\log_{10} K = 56.756$.

[3] Jakowkin: Z. physik. Chem. **29**, 637 (1899); Boericke: Loc. cit., p. 63.

[4] Loc. cit., p. 1047.

which are not based on measurements used above, so as to avoid working in a circle.

The values of the free energy computed in this way are given in column 4 of Table XXVIII.

7. THE FREE ENERGY OF MERCURIC CHLORIDE, BROMIDE, AND IODIDE.

If the equilibrium between a metal and two of its halides in different states of oxidation is known, the free-energy change attending the decomposition of the lower halide into the higher halide and the metallic element may be computed, and this combined with the free energy of the lower halide, gives that of the higher one. The necessary data exist in the case of the mercury halides, since the concentration of each mercuric halide (as such) in equilibrium with the corresponding solid mercurous halide and mercury has been indirectly determined by Sherrill.[1] If that concentration be designated by C and the solubility of the mercuric halide (regarded as nonionized and unassociated) by S, then the work producible by the reaction

$$Hg_2X_2(\text{solid}) = Hg + HgX_2(\text{solid})$$

may be readily shown[2] to be $RT \log_e C/S$. And evidently the algebraic sum of this quantity of work and of that attending the production of one formula weight of Hg_2X_2 out of its elements is the free-energy decrease attending the formation of one formula weight of HgX_2 out of its elements.

The values of the quantities C and S given by Sherrill, of the calculated quantity of work $RT \log_e C/S$, and of the free energy in calories of the mercuric halides are given in the following table.

[1] Z. physik. Chem. 47, 103 (1904).

[2] In a reaction mixture consisting of mercury and solid mercurous halide in equilibrium with an aqueous solution of mercuric halide of concentration C, let one formula weight of solid Hg_2X_2 decompose into mercury and (dissolved) HgX_2, the latter being simultaneously removed at the same concentration into pure water through a wall permeable for it alone. The work produced hereby is RT. Now concentrate the HgX_2 solution so obtained till its concentration becomes S, that of a saturated solution: the work produced is $RT \log_e C/S$. Finally force the salt out of the solution in the solid state: the work produced is $-RT$. The total work is therefore $RT \log_e C/S$.

TABLE XXV.—FREE ENERGIES OF MERCURIC CHLORIDE, BROMIDE AND IODIDE.

Substance.	$C \times 10^6$ in mols per l.	$S \times 10^3$ in mols per l.	$RT \log_e C/S$.	Free energy $\times(-1)$.
$HgCl_2$	2.9	260.0	—6750	42600
$HgBr_2$	2.4	17.0	—5250	37300
HgI_2	4.0	0.13	—2060	24100

8. THE FREE ENERGY OF WATER, AMMONIA, HYDROGEN CHLORIDE, AND HYDROGEN BROMIDE.

Hydrogen | Liquid Water | Oxygen.

As stated above, the best value for the electromotive force of this cell seems to be 1.22 volts at about 20°. The corresponding value of the free energy of one mol of water calculated by the equation $F = -[2EF - 1.5RT]$ is 55,500 calories.

Hydrogen | Hydrochloric Acid | Chlorine.

The free energy formula $F = -(\nu EF + \Delta NRT)$, given in Section 1 of this article that applies to a solid in contact with its saturated solution applies equally well to a gas in equilibrium with its solution (it being understood that ΔN represents the increase in the number of mols of gas attending the reaction). Thus, if we have a hydrogen and a chlorine electrode in normal hydrochloric acid, the electromotive force of this cell would give the free energy of hydrochloric acid at a pressure equal to its partial pressure over its normal solution, referred to hydrogen and chlorine at atmospheric pressure. The term ΔN becomes zero, as there are as many mols of gas before as after the reaction has taken place. If, however, we wish to know the free energy of hydrochloric acid at atmospheric pressure, referred to hydrogen and chlorine at atmospheric pressure, then the free energy computed from the voltage must be diminished by $RT \log_e 760/p$, where p is the partial pressure in millimeters of mercury of hydrochloric acid over the solution in question. The necessary measurements of vapor-pressure and electromotive force have been made for hydrochloric and hydrobromic acids, but not for hydriodic acid.

Dolezalek[1] has measured the cell H_2 | HCl | Cl_2 at 30° and at different concentrations. He has also measured the partial pressures of hydrochloric acid at the same temperature, for different concentrations. The following table contains these results, and in the last column the free energy computed from them.

[1] Z. physik. Chem. 26, 321 (1898).

TABLE XXVI.—DATA FOR HYDROCHLORIC ACID AND ITS FREE ENERGY.

Equivalents per liter.	Partial pressure in mm. of Hg 30°.	E.m.f. in volts.	Free energy × (—1) of one mol at 30°.
4.98	0.24	1.190	22,800
6.43	0.69	1.147	22,400
11.20	134.0	1.005	22,200
11.62	189.0	0.999	22,300
12.14	313.0	0.981	22,100
12.25	337.0	0.974	22,000

The average value is 22,300 calories ±0.5 per cent., at 30°. The heat of the reaction ($-U$) is 22,000[1] calories at 18°, and varies very slightly with the temperature. It would be practically the same at 30°. The temperature coefficient of the free energy F at 30° is then $\frac{dF}{dT}=\frac{F-U}{T}=1.07$ calories per degree. The free energy at 18° would then be only 1.8 calories less than that at 30°. This correction is, therefore, negligible.

Hydrogen | Hydrobromic Acid | Bromine.

Measurements of the above cell have been made by Bodenstein and Geiger[2] at 30°, as well as of the vapor-pressures of the hydrobromic acid over the solutions and of the hydrogen and the bromine. The bromine couple was not saturated with bromine. The electromotive force of this cell gives the free energy of hydrobromic acid at the partial pressure measured, formed from gaseous bromine and hydrogen at the measured pressures.

If we start with gaseous bromine at atmospheric pressure (assuming this degree of supersaturation could be realized), this must be expanded to the pressure at which it exists in the cell. The work done by the system will be $0.5\ RT \log_e \frac{760}{P_{Br_2}}$ for one-half of a mol. Allowing the hydrogen to change from atmospheric pressure to that measured, the work done by the system will be $0.5\ RT \log_e \frac{760}{P_{H_2}}$. Now compressing the acid to atmospheric pressure, the work done by the system will be $-RT \log_e \frac{760}{P_{HBr}}$. Hence the free energy is given by the formula:

$$-F = E \times 23090 + 0.5\ RT \log_e \frac{(P_{HBr})^2}{(P_{Br_2})(P_{H_2})}.$$

[1] Ostwald: Lehrbuch allg. Ch. 2te Aufl. Bd. II, 1, p. 103.

[2] Z. physik. Chem. 49, 70 (1904).

The following table gives the data for this computation, the final column containing the free energy itself.[1]

TABLE XXVII.—DATA FOR HYDROBROMIC ACID AND ITS FREE ENERGY.

Partial pressure in mm. of mercury.			E.m.f. in volts.	Free energy ×(—1).
HBr.	Br_2.	H_2.		
12.0	0.682	742.5	0.573	12850
2.25	1.509	753.6	0.625	12800
1.19	1.448	760.6	0.636	12680

The average value is 12,800 calories at 30°. The difference in the heat capacities at constant volume of one mol of hydrobromic acid and of its constituents is 1.06 calories.[2] The heat of the reaction is, therefore, practically the same for 30°. In order to get the free energy at 18° we may substitute the known values in the integrated Second Law equation given below (see under Ammonia). This gives at 18° F=—11950 calories.

Hydrogen | Ammonia | Nitrogen.

The cell $Pt+H_2$ | solid NH_4NO_3+solution of NH_4NO_3 in NH_3 | $Pt+N_2$ is stated by Baur to be reversible and to have at —10° an electromotive force of 590 millivolts.[3] The partial pressure p of the ammonia over this mixture has been found to be 240 mm. at —10.5°.[4] Now the free energy (F) of one mol of gaseous ammonia at atmospheric pressure referred to its elements at atmospheric pressure (p_o) is given by the expression,

$$-F=3EF-RT+RT \log_e p/p_o,$$

from which by substituting the above values one finds at —10° F=—39,700 calories.

In order to obtain from this the free energy at 18° we may employ the Second Law equation $\frac{dF}{dT}=\frac{F-U}{T}$, which, integrated under the assumption that the energy increase (U) attending the reaction is constant, gives $\frac{F_2}{T_2}-\frac{F_1}{T_1}=-U\left[\frac{1}{T_1}-\frac{1}{T_2}\right]$. U, however, has the value —11,420 calories at 18° and —11,280 calories at —10°, or an average value of —11,350 calories.[5]

[1] Subsequently to sending this article to the Journal, it was found that calculations of the free energy of hydrochloric and hydrobromic acids had previously been published by Haber in his book "Thermodynamik technischer Gasreaktionen."

[2] Obtained from Landolt-Börnstein-Meyerhoffer's tables.

[3] Baur: Z. anorg. Chem. **29**, 305 (1902).

[4] Kuriloff: Z. physik. Chem. **25**, 108 (1898).

[5] Ostwald: Loc. cit., p. 139.

Putting $F_1 = -39{,}700$, $T_1 = 263$ and $T_2 = 291$ we find for F_1 (which is the free energy of one mol gaseous NH_3 at 18° and one atmosphere pressure) the value of —45,200 calories.

This result may be compared with that obtained by using the equilibrium constant of the reaction in question recently obtained for the temperature 1020° by Haber and Van Oordt.[1] At this temperature, this constant, which is defined by the equation

$$K = \frac{(P_{N_2})^{0.5} \quad (P_{H_2})^{1.5}}{(P_{NH_3})},$$

has, when the pressure is expressed in atmospheres, the value 2706. From this value the work producible by the reaction

$$0.5N_2 + 1.5H_2 = NH_3$$

when it takes place from left to right and when each gas is at atmospheric pressure is calculated by the equation given in Section I of this article to be —23,000 calories. By means of the heat of reaction and heat capacity data cited by the authors and the integrated form of the Second Law equation given by them the work produced may be computed for any other temperature. For 18° it is found to be +5100. Hence we have for the free energy of one mol of ammonia, $F = -5100$ calories.

This result is evidently utterly inconsistent with the value deduced from potential measurements. The most probable explanation seems to be that there is an error in the interpretation of the potential values arising from the fact that the potential observed was not determined by the solution-tendency of nitrogen at all, but by some other reaction in the solution. Nitrogen is a very inert gas, especially at low temperatures; and therefore this seems a reasonable explanation. There does not seem to be any corresponding possibility of a large error in the computation involving the equilibrium constant, and it is probable that the value of the free energy deduced therefrom is at least an approximate one. Both are given in Table XXIX.

9. SUMMARY OF THE RESULTS.

The results of the above-described computations as well as certain other related data are presented in Table XXVIII. Column 2 contains the free energies of the chlorides referred to gaseous chlorine at atmospheric pressure. These values are here collected from the various preceding tables. By adding $N R T$ to these

[1] Z. anorg. Chem. 44, 341 (1905).

the values in column 3 for the chlorides are obtained, which show what their free energies would be if the chlorine were liquid or solid at the temperatures in question. The previously computed free energies of bromides and iodides are also given in this column. The free energies computed from solubilities are given in column 4. The values that deviate widely from those in column 3, which is the case with the most difficultly soluble compounds where the error in determining the solubility is large, are placed in brackets. The next three columns contain the values of the total energies, all of which are taken from the third edition of Landolt-Börnstein-Meyerhoffer's Tables. Column 5 contains the total energy of the chlorides with respect to gaseous chlorine. From this value the heat of vaporization (2200 calories for one atomic weight)[1] has been subtracted, and the so obtained total energies referred to liquid chlorine are given in column 6, as are also the total energies of the bromides referred to liquid bromine. Column 7 contains the total energies referred to the halogens as solids. In the case of the bromides, the heat of fusion of bromine at its melting-point —7.3° (1300 calories) has been subtracted from the value given in column 7 to get the total energy referred to solid bromine. The heat of fusion of chlorine has not been determined, but as an approximate basis of comparison the heat of fusion has been assumed identical with that of bromine, which seems justifiable since bromine and iodine differ but little. These values are of course fictitious ones, since solid chlorine and bromine cannot exist at 18°; they are, therefore, enclosed in parentheses. They represent what the total energies would be if the solid elements were superheated to 18° and there had the same heat of fusion as at lower temperatures. In the case of the mercury halides, the total energy is given in the seventh column with respect both to solid and to liquid mercury, the heat of fusion (600 calories) being assumed identical with that at the melting-point.

Column 8 contains the ratio of the free to the total energies referred to the elements in the solid state, while column 9 gives the same ratio for the elements in the ordinary state. (For the chlorides this is the ratio of values in column 2 to those in column

[1] It is not clear whether this value which is cited as a private communication from Knietsch includes the external work, but this would make a difference of only about 300 cal.

TABLE XXVIII.—THE FREE AND TOTAL ENERGIES OF THE SOLID HALIDES OF SILVER, MERCURY, COPPER, THALLIUM, AND LEAD AT ABOUT 18°.

Formula of compound. 1.	Free energy × (−1). Halogen gaseous at atmos. pres. 2.	Free energy × (−1). Halogen liquid or solid. 3.	Free energy × (−1). Halogen in usual state computed from solubilities. 4.	Total energy × (−1). Halogen gaseous. 5.	Total energy × (−1). Halogen liquid. 6.	Total energy × (−1). Halogen solid. 7.	Ratio of free to total energy. Elements solid. 8.	Ratio of free to total energy. Elements in usual state. 9.	Solubility at 20° in equivalents per liter. 10.
AgCl	25600	25900	26800[6]	28900	26700	(25400)	1.02	0.89	1.06×10^{-5}
AgBr	....	23000	23900	....	23400[1]	(22100)	1.04	0.98	5.1×10^{-7}
AgI	....	15900	[26300]	....	....	14200[1]	1.12	1.12	1.5×10^{-8}
CuCl	27800	28100	....	33800	31600	(30300)	0.93	0.82	.....
CuBr	....	23700	....	....	25000	(23700)	1.00	0.95	.....
CuI	....	16600	....	....	....	16600	1.00	1.00	.....
TlCl	43200	43500	43700	48300	46100	(44800)	0.97	0.89	1.39×10^{-2}
TlBr	....	39600	39700	....	41300	(40000)	0.99	0.96	1.64×10^{-3}
TlI	....	....	29900	....	....	30200	0.99	0.99	1.92×10^{-4}
Hg_2Cl_2	49400	50000	52100	62000	57600	(55000)[3] (53800)[4]	0.93	0.80	1.6×10^{-6}
Hg_2Br_2	....	42800	42900	....	49000[3]	(46400)[3] (45200)[4]	0.95	0.88	1.4×10^{-7} [2]
Hg_2I_2	....	26800	[46400]	....	....	28800[3] (27600)[4]	0.97	0.93	6.1×10^{-10} [2]
$HgCl_2$	....	43200[5]	42600	52600	48200[3]	(45600)[3] (45000)[4]	0.96	0.81	5.26×10^{-1} [2]
$HgBr_2$	....	....	37300	....	40500[3]	(37900)[3] (37300)[4]	1.00	0.92	3.4×10^{-2} [2]
HgI_2 (red)	....	....	24100	....	....	25100[3] (24500)[4]	0.98	0.96	2.6×10^{-4} [2]
$PbCl_2$	74800	75400	74300	82700	78300	(75700)	1.00	0.90	7.14×10^{-2}
$PbBr_2$	....	64200	62300	....	64500	(61900)	1.04	1.00	4.64×10^{-2}
PbI_2	....	41700	42300	....	....	39800	1.05	1.05	2.98×10^{-3}

[1] Berthelot's value. [2] At 25°. [3] Mercury liquid. [4] Mercury solid. [5] Computed from column 4.

[6] Using Lewis' recent determination of the electrolytic potential of silver, the values for the chloride, bromide and iodide are 26500, 23300 and [27000]. See this Journal, **28**, 158 (1906).

5); column 10 gives the values of the solubilities used in computing column 4.

All energy values are in gram-calories, are for one formula weight of salt as shown in the first column, and are based on the convention that the energy of the elements (considered gaseous, liquid or solid as shown) is zero. The chlorine when gaseous is at atmospheric pressure.

Table XXIX contains the results for other compounds than the halides, and needs no explanation.

TABLE XXIX. — THE FREE AND TOTAL ENERGIES OF THE OXIDES OF SILVER AND MERCURY, OF WATER, AMMONIA, HYDROCHLORIC AND HYDROBROMIC ACIDS AT ABOUT 18°.

Compound.	Free energy ×(—1).	Total energy ×(—1).	Ratio of free to total energy.
Hg_2O	13400	22200	0.60
Ag_2O	3900	5900	0.66
Ag_2O[1]	3310	5900	0.56
H_2O (liquid)	55500	67600	0.82
H_2O[2]	53800	57500	0.93
HCl[2]	22300	22200	1.01
HBr[2]	11950	8400	1.42
NH_3[2] (Baur)	45200	11400	4.00
NH_3[2] (Haber)	5100	11400	0.45

10. DISCUSSION OF THE RESULTS.

First may be noted the good agreement between the free energy values of column 2 or 3 and those of column 4 in Table XXVII, the differences between which seldom exceed 4 per cent. The two series of values are based upon independent data, except that the same measurements of potentials of the halogen electrodes against halide solutions are to a great extent involved in both calculations. Except with respect to this last factor, the agreement is therefore a confirmation of the accuracy of the results. To this agreement there are two pronounced exceptions, namely in the case of the iodides of silver and mercurous mercury, where the free energies calculated from solubilities and electrolytic potentials against normal solutions of the ions exceed

[1] This is the free energy computed from Lewis' recent value of the decomposition-pressure of silver oxide. (See this Journal, 28, 158, (1906)).

[2] Compounds gaseous at atmospheric pressure. In the case of water this condition is, of course, unrealizable at 18°, but the computed values represent, nevertheless, approximately what the energies would be if water-vapor were supersaturated to that extent.

are 26500, 23300 and [27000]. See this Journal, 28, 158 (1906).

those calculated from the electromotive force of cells with the salts present as solid phases by 65 and 73 per cent. The explanation of this extraordinary disagreement is by no means obvious; it can not be due to an error in the electrolytic potential of the iodine electrode, for this is in substance common to both calculations, nor to one in that of the silver or mercury electrode, for this would have produced disagreement also in the cases of the chlorides and bromides of these elements; it is moreover difficult to believe it is due to an error in the potentials of the metals against the saturated solutions, since these values are based on fairly concordant measurements by different observers —five in the case of silver iodide, two in the case of mercurous iodide (see Tables X and XIII); and finally it can hardly be due to error in the solubilities, for in order to give values of the free energy identical with those computed from the potentials against the saturated solutions it would be necessary to assume for these two iodides solubilities (1.1×10^{-4} for AgI, 7.8×10^{-5} for Hg_2I_2) greater than those for the corresponding chlorides (1.06×10^{-5} for AgCl, 1.6×10^{-6} for Hg_2Cl_2) which is well-known not to be the case. The most probable explanation of the discrepancy would seem to be that there exists in the solutions of these iodides complex ions which make the computation from their solubilities uncertain. However this may be, from every point of view the free energy computed in the other way seems more reliable: first, because it does not involve any theoretical assumptions; second, because its values correspond for these two salts far better with those of the total energy (see below); and third, because they fall in line with those for the corresponding chlorides and bromides. Another point worthy of mention in connection with the two sets of free energy values is that in case of mercurous chloride and bromide these agree more closely when the salts are assumed to be tri-ionic ones of the formula $(Hg_2)Cl_2$ or $(Hg_2)Br_2$ rather than di-ionic ones of the formula HgCl or HgBr. Thus the values calculated from the solubilities under the former assumption are (as given in the table) 52,100 for the chloride, 42,900 calories for the bromide, and under the latter assumption 60,600 and 53,400 calories respectively, while the values computed from the potentials against the saturated solutions are 49,400 and 42,800 calories respectively.

In regard to the magnitude of the free energies of the different compounds the following approximate regularities will be seen to exist.

(1) In the case of these solid halides, the chloride has a free energy uniformly greater than that of the corresponding bromide by from 2500 to 5500 calories per equivalent, and the bromide has a free energy greater than that of the corresponding iodide by 7000 to 11,000 calories per equivalent.

(2) The corresponding halides of mercurous mercury, silver, and cuprous copper have free energies which differ from each other by less than 3500 calories per equivalent, but which increase slightly in every case in the order mercury, silver, and copper.[1]

The most important general conclusion to be drawn from these results relates, however, to the connection between the free and total energies. It will be seen from column 8 of Table XXVIII that *the ratio of the free to the total energy of these solid salts when these energies are referred to those of the elements in the solid state as zero does not differ from unity by more than 7 per cent.*, except in the single instance of silver iodide. This principle, which is of great importance since it enables for approximate purposes the usually well-known heat of formation to be employed in the place of the often unknown free energy in the study of the equilibrium of reactions involving solid substances, has not previously been so extensively tested and confirmed.

An examination of the last five rows of values in Table XXIX shows that for gaseous water and hydrochloric acid, produced out of the gaseous elements, the ratio of free to total energy is not far from unity, but that it has widely divergent values in the case of the other gaseous substances, indicating the absence of any simple relations.

The author wishes here to express his very sincere thanks to

[1] This will be more obvious from the following summary of the free energies per equivalent of salt:

	Cl.	Diff.	Br.	Diff.	I.	Diff.
Hg(ous)	24700		21400		13400	
		900		1600		2500
Ag	25600		23000		15900	
		2500		700		900
Cu(ous)	28100		23700		16600	

Prof. A. A. Noyes for the valuable advice received while carrying out this work. Without this advice it would not have arrived at its present state.

ROGERS LABORATORY OF PHYSICS,
MASSACHUSETTS INSTITUTE OF TECHNOLOGY,
March, 1906.

[CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 11.]

ON THE APPLICABILITY OF RAOULT'S LAWS TO MOLECULAR WEIGHT DETERMINATIONS IN MIXED SOLVENTS AND IN SIMPLE SOLVENTS WHOSE VAPOR DISSOCIATES.

BY GILBERT NEWTON LEWIS.

Received March 23, 1906.

BECKMANN[1] has recently determined the molecular weights of several substances in concentrated sulphuric acid by the boiling-point method. Now the researches of Deville and Troost have shown that the vapor of sulphuric acid is completely dissociated into water and sulphur trioxide, and the question arises as to whether it is justifiable to apply to a case of this kind the simple laws of Raoult for the lowering of the vapor-pressure and the raising of the boiling-point.

The solvent used by Beckmann is described as follows: "Zu allen Versuchen wurde die verwendete reine Schwefelsäure aus einer Glasretorte fraktioniert destilliert. Nur der konstant bei 331.7° (unkorrigiert) übergehende mittlere Teil fand Verwendung." This sulphuric acid of constant boiling-point contains about 1.5 per cent. of water and must therefore be regarded, not as a simple liquid, but as a binary mixture. If instead of regarding it as a mixture of sulphuric acid and water we regard it as a mixture of sulphur trioxide and water, it is obvious that it does not differ essentially from any other binary mixture (such as a 20 per cent. hydrochloric acid solution for example) which has a constant boiling-point.

The following thermodynamic considerations lead to the interesting conclusion that, while pure sulphuric acid cannot be used for molecular weight determinations, the use of the constant boiling acid employed by Beckmann is entirely justifiable. In-

[1] Z. physik. Chem. 53, 129 (1905).

deed we shall find that the familiar equation for the molecular elevation of the boiling-point of a simple liquid may be applied equally well to any constant boiling mixture, composed of any number of constituents.

The equations of Raoult for the lowering of the vapor pressure and the raising of the boiling-point of a simple liquid may be written as follows:

$$N\frac{dp}{p} = -dn \qquad (1)$$

$$d'T = \frac{RT^2}{Q}dn \qquad (2)$$

In (1) dp is the change in vapor-pressure when dn gram-molecules of solute are added to N gram-molecules of solvent. In (2) Q is the heat of vaporization of that quantity of the solvent in which dn gram-molecules of the solute are dissolved, $d'T$ is the change in boiling-point.

Corresponding to equation (1) Nernst[1] has obtained for a binary solvent the equation,

$$N_1\frac{dp_1}{p_1} + N_2\frac{dp_2}{p_2} = -dn, \qquad (3)$$

where p_1 and p_2 are the two partial vapor-pressures from a mixture containing N_1 gram-molecules of the first substance and N_2 of the second, and dp_1 and dp_2 are the changes in these partial pressures caused by dissolving in the mixture dn gram-molecules of a third substance.

In general, it is impossible to predict from this equation the change in the total vapor-pressure of the solvent when a given quantity of solute is added, but in the special case of a constant boiling solvent the equation may be simplified. It is a well-recognized fact that a constant boiling mixture must always have the same composition as the vapor phase with which it is in equilibrium. In such a case therefore

$$\frac{p_1}{p_2} = \frac{N_1}{N_2}$$

or by the principles of proportion,

$$\frac{N_1}{p_1} = \frac{N_2}{p_2} = \frac{N_1+N_2}{p_1+p_2}. \qquad (4)$$

Combining this equation with equation (3) gives

[1] Z. physik. Chem. 11, 1 (1893).

$$\frac{N_1+N_2}{p_1+p_2}(dp_1+dp_2)=-dn.$$

Now the total vapor-pressure, P, of the liquid is equal to p_1+p_2, hence the last equation may be written,

$$(N_1+N_2)\frac{dp}{p}=-dn, \qquad (5)$$

which is the same as equation (1).

Similarly, it may be shown that the first law of Raoult is applicable to a constant boiling mixture of any number of constituents.[1]

If in place of the sulphuric acid of constant boiling-point we consider pure sulphuric acid, that is, a mixture of water and sulphur trioxide such that $N_1=N_2$, then obviously equation (3) may be somewhat simplified but does not yield equation (1) and therefore to such a solvent Raoult's law cannot be applied.

Turning now from the lowering of the vapor-pressure to the raising of the boiling-point, we have a more complex problem.[2] Let us obtain first a general equation for the elevation of the boiling-point of any binary solvent.

Starting with a mixture containing N_1 gram-molecules of the first substance and N_2 of the second, in equilibrium with an infinitesimal quantity of the vapor-phase, at the boiling-point, let us add dn gram-molecules of a third substance and allow the temperature to rise to the new boiling-point, that is, until the total vapor-pressure is again equal to the original external pressure. If p_1 and p_2 represent the original vapor-pressures, and dp_1 and dp_2 their changes, then, since the total vapor-pressure is the same after the change as before,

$$dp_1+dp_2=0. \qquad (6)$$

The changes in p_1 and p_2 are caused in part by the addition of the solute and in part by the change in temperature. We may consider these effects separately and write,

$$dp_1=d_1p_1+d_2p_1,\ dp_2=d_1p_2+d_2p_2 \qquad (7)$$

[1] This conclusion is of course valid only when the vapor of each constituent is normal and when the molecular weights in the vapor state are used in calculating the number of gram-molecules of the solvent.

[2] This problem has been discussed by Nernst (loc. cit.) with the aid of the provisional assumption that the addition of the solute causes the same percentage lowering of the two partial vapor-pressures of the binary solvent, but the experimental work of Nernst and Roloff (Z. physik. Chem. 11, 7 (1893)) showed the incorrectness of this assumption.

where d_1p_1 and d_1p_2 are the changes produced merely by the addition of the solute; d_2p_1 and d_2p_2, by the change in temperature. For these changes we have the following equations:

$$N_1\frac{d_1p_1}{p_1}+N_2\frac{d_1p_2}{p_2}=-dn. \tag{8}$$

$$N_1\frac{d_2p_1}{p_1}+N_2\frac{d_2p_2}{p_2}=\frac{Q}{RT^2}dT. \tag{9}$$

The first of these equations is that of Nernst which we have used above. The second[1] shows the influence of temperature on the vapor-pressures of a binary mixture, when dT is the change in temperature and Q the total heat of vaporization of the mixture containing N_1 gram-molecules of the first substance and N_2 of the second.

Adding these two equations we have,

$$N_1\frac{d_1p_1+d_2p_1}{p_1}+N_2\frac{d_1p_2+d_2p_2}{p_2}=\frac{Q}{RT^2}dT-dn,$$

or by equation (7),

$$N_1\frac{dp_1}{p_1}+N_2\frac{dp_2}{p_2}=\frac{Q}{RT^2}dT-dn.$$

Hence by equation (6),

$$\left(\frac{N_1}{p_1}-\frac{N_2}{p_2}\right)dp_1=\frac{Q}{RT^2}dT-dn. \tag{10}$$

This equation cannot be further simplified except with the aid of special assumptions. Evidently, therefore, the change in boiling-point does not depend solely upon the number of gram-molecules of solute. It can be predicted only when the effect of the solute upon the partial vapor-pressure of one of the constituents of the mixture is also known. In general therefore, we cannot speak of the molecular lowering of the boiling-point in the case of a binary solvent, since equivalent quantities of two different solutes may have very different effects on the boiling-point. In fact one solute may raise the boiling-point and another lower it.

When, however, we consider the special case of a constant boiling mixture a great simplification of equation (10) is possible, for then, as we have seen in equation (4), $\frac{N_1}{p_1}=\frac{N_2}{p_2}$, the first

[1] The equation in this form is, I believe, new. It is a simpler form of an equation obtained by Nernst ("Theor. Chem." (4th Edition), p. 117). The proof of it will be given in another place.

member of equation (10) becomes zero, and we have

$$dT = \frac{RT^2}{Q}\, dn, \qquad (11)$$

which is equation (2).

In the same way it may be proved that Raoult's law for the raising of the boiling-point applies to any constant boiling mixture, of any number of constituents.

In deriving equation (11) we have implicitly made use of two assumptions. The first is contained in equation (8) and is merely the assumption that the solute dissolves to form an ideal solution. The second is contained in equations (8) and (9). It is the assumption that the vapor obeys the gas laws. Now while the first assumption is fundamental and necessary, it is possible by a somewhat more general method than the one here adopted to dispense with the second assumption, and thus to show that equation (11) applies to all solvents, even to those whose vapors behave abnormally.

Our general conclusions are therefore as follows:

(1) The law of Raoult for the lowering of the vapor-pressure is applicable to an ideal dilute solution in any constant boiling mixture whose vapor obeys the gas laws.

(2) The law of Raoult for the raising of the boiling-point is applicable to an ideal dilute solution in any constant boiling mixture whatever.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

A REVISION OF THE ATOMIC WEIGHT OF CADMIUM.

BY GREGORY PAUL BAXTER, MURRAY ARNOLD HINES AND HARRY LOUIS FREVERT.

Received April 2, 1905.

(SECOND PAPER.)

FROM a recent investigation of the atomic weight of cadmium[1] the value 112.469 (Ag = 107.930) for this constant was obtained, by analysis of cadmium chloride. Since this value is nearly one-tenth of a unit higher than the results of recent prior determinations by other investigators, in order to confirm or disprove the higher value, the analysis of cadmium bromide was undertaken.

[1] Baxter and Hines: This Journal, 27, 222 (1905).

PURIFICATION OF MATERIALS.

In the previous investigation the cadmium material was purified by fractionally precipitating cadmium sulphide with hydrogen sulphide from an acid solution of cadmium chloride. Two small fractions were rejected, and the next three, which included very nearly all the remainder of the cadmium, were preserved separately. Each one of these three fractions was first thoroughly washed, then dissolved in hydrochloric acid and reprecipitated. Next the precipitates were again dissolved, in nitric acid, the nitric acid was expelled by heating with an excess of sulphuric acid, and the sulphate was recrystallized thrice from pure water. Fraction I and a portion of Fraction II were converted into chloride and were analyzed in the earlier work, while Fraction III and a second portion of Fraction II were converted into bromide.

The method employed for this purpose was that of depositing metallic cadmium electrolytically, dissolving the metal in bromine under water in a quartz dish, and recrystallizing the bromide in platinum vessels. In the first experiments electrolysis was carried on in a solution of the sulphate in pure water, between two electrodes of platinum foil. A sponge of extremely small crystals was thus produced. These crystals contained occluded sulphate in considerable quantities, and no amount of washing with water was sufficient completely to leach out this occluded material. Hence the bromide made from this metal was seriously contaminated with sulphate, which was finally eliminated with difficulty by repeated crystallization. This bromide was used only in preliminary experiments. More satisfactory results were obtained by depositing the metal upon a platinum dish which had been covered with a very thin film of soft paraffine, so that the deposit could be readily separated from the dish.[1] The cadmium was first washed with water, then with ether, next with alcohol, and finally with water again. This treatment effectually cleansed the metal from paraffine. In order to convert the cadmium into bromide, it was covered in a quartz dish with water slightly acidified with hydrobromic acid to prevent the formation of basic cadmium salts, and the purest bromine was added in small quantities until the metal was almost wholly dissolved. The solution was heated with the residual metallic cadmium upon a

[1] Richards: Pr. Am. Acad. 25, 200 (1890).

steam-bath until every trace of bromine had disappeared. Then it was filtered with a platinum funnel into a platinum dish, and was recrystallized three times, with centrifugal drainage in the platinum funnel after each crystallization.[1] The original solution contained only traces of sulphate, and, when tested with barium hydroxide, the mother-liquors of the third crystallization gave absolutely no test for sulphate, hence the crystals themselves must have been pure (Samples II*a* and III*a*). From the mother-liquors of each fraction, by three crystallizations, similar samples were obtained (Samples II*b* and III*b*). The crystals were dried over potassium hydroxide in a vacuum desiccator.

Commercial bromine was freed from chlorine by two distillations from a concentrated solution of a bromide, the bromide in the second distillation being almost free from chloride. The bromine was covered with water, and hydrogen sulphide, which had been thoroughly washed with water, was passed into the solution until reduction of the bromine was complete. The solution was boiled, after mechanical separation of the greater part of the free sulphur and bromide of sulphur, and was filtered. Iodine was eliminated by boiling the hydrobromic acid with several small portions of potassium permanganate and rejecting the bromine set free. By heating the remainder of the hydrobromic acid with an excess of permanganate, over half of the bromine was obtained in the free state. The process of reduction with hydrogen sulphide and oxidation with permanganate was then repeated with the resulting bromine, and the final product was redistilled shortly before use.

One sample of silver was purified especially for this research. The processes to which it was subjected were essentially those which have been repeatedly used in this laboratory for the purification of silver. The commercial metal was dissolved in nitric acid, and the solution was filtered and precipitated at considerable dilution with hydrochloric acid. After thorough washing, the precipitate was reduced with invert sugar and sodium hydroxide, and the metallic silver was fused with a blowpipe on a crucible of the purest lime. In order to cleanse the buttons from surface impurities, they were first scrubbed with moist sand, and then the surface was removed with dilute nitric acid. Next the buttons were dissolved in nitric acid and the solution was reduced

[1] Richards: This Journal, 27, 110 (1905).

with ammonium formate.[1] The precipitated silver was thoroughly washed and again fused in a lime crucible. The final process of purification consisted in electrolyzing the silver, with a solution of silver nitrate, made from a portion of the silver, acting as electrolyte, while the anode was a pile of the pure silver buttons and the cathode a bar of the purest silver. The electrolytic crystals were washed, dried, and fused in a current of pure hydrogen on a lime boat. The buttons were cleansed with dilute nitric acid, and, after drying at 200°, they were cut into fragments with a clean chisel and anvil. Then they were again treated with fresh portions of dilute nitric acid until free from iron, washed, dried, and finally heated to about 400° in a vacuum. This silver was employed in analyses 4 to 8.

In the first three analyses a mixture of two specimens of silver was employed, both of which had already been used in an investigation upon the atomic weight of iodine by one of us.[2] One was prepared from silver nitrate which had been seven times recrystallized from nitric acid, five times recrystallized from water, and finally precipitated with ammonium formate. The other was precipitated once as silver chloride, electrolyzed once, and finally reduced with ammonium formate.

Water was purified by double distillation with tin condensers, first with alkaline permanganate, finally with a trace of sulphuric acid. Nitric acid was twice distilled with a platinum condenser, the first third of the distillate being rejected in both distillations. The product of the first distillation contained only the merest trace of chlorine.

METHOD OF ANALYSIS.

The method of analysis was essentially that already frequently employed in this laboratory for the analysis of metallic halides. Weighed portions of the bromide, after fusion in nitrogen and hydrobromic acid gases, were first titrated against weighed portions of silver. Then the precipitated silver bromide was collected and weighed.

The apparatus used for the fusion of the salt in hydrobromic acid gas was employed in the preparation of ferrous bromide

[1] Richards: Publications of the Carnegie Institution, No. 28, p. 19 (1905); This Journal, **27**, 475.

[2] Baxter: Pr. Am. Acad. **41**, 73 (1905).

by one of us,[1] and is a modification of apparatus used for a similar purpose in the determination of the atomic weights of cobalt,[2] nickel,[3] and uranium[4] in this laboratory. A mixture of air and ammonia was passed over heated rolls of copper gauze and the excess of ammonia was removed by means of sulphuric acid. The gas was then conducted into an apparatus constructed wholly of glass, with ground joints, which consisted of a tower filled with beads moistened with silver nitrate solution to remove sulphur compounds, two similar towers containing dilute sulphuric acid to eliminate last traces of ammonia, and two towers filled with sticks of fused potassium hydroxide to absorb moisture and carbon dioxide. The partially dried gas, after bubbling through bromine in a small flask, passed into a second flask containing concentrated hydrobromic acid solution in which washed red phosphorus was suspended, to convert the bromine into hydrobromic acid. A U-tube, also containing red phosphorus and hydrobromic acid, removed traces of bromine which escaped reduction in the flask. Two additional U-tubes containing beads moistened with concentrated hydrobromic acid only, served to eliminate phosphorus compounds which were found, in the investigation upon ferrous bromide,[5] to accompany the hydrobromic acid if the phosphorous acid in the reduction flask was allowed to become very concentrated. Finally, the mixture of nitrogen and hydrobromic acid gases was thoroughly dried, first by pure fused calcium bromide, and then by resublimed phosphorus pentoxide.

The cadmium bromide, contained in a weighed platinum boat, was heated gently in a current of nitrogen until a small quantity of residual crystal water was expelled, then strongly in a current of nitrogen and hydrobromic acid until fused. After the salt had cooled, the hydrobromic acid was displaced by nitrogen and this in turn by dry air. The boat was then transferred to the weighing-bottle in which it was originally weighed, and the stopper was inserted without an instant's exposure of the salt to moisture, by means of the bottling apparatus which has been

[1] Baxter: Pr. Am. Acad. 39, 246.
[2] Richards and Baxter: Ibid. 33, 117.
[3] Richards and Cushman: Ibid. 33, 99.
[4] Richards and Merigold: Ibid. 37, 378.
[5] Loc. cit.

frequently described in papers from this laboratory.[1] The weighing-bottle was then allowed to stand in a desiccator near the balance case for some time before it was weighed.

Next the boat was transferred to a flask and the salt was dissolved in about 300 cc. of the purest water. The weighing-bottle was rinsed and the rinsings were added to the solution. Then the solution was filtered into the glass-stoppered precipitating flask through a tiny filter to collect a trace of insoluble matter, and the filter-paper and residue were ignited at a low temperature in a weighed porcelain crucible. This residue, which usually amounted to less than 0.1 mg. and was never as much as 0.2 mg., did not contain detectable quantities of cadmium, and probably consisted of silica and a trace of platinum removed from the boat during the fusion, for the boat, when reweighed, in most cases was found to have lost a few hundredths of a milligram. No change in weight could be found when the boat was first dried and weighed, then ignited and reweighed. The difference between the weight of the residue and the loss in weight of the boat was subtracted from the weight of the cadmium bromide.

From the corrected weight of the cadmium bromide very nearly the requisite quantity of pure silver was calculated. This silver was weighed out and dissolved, in a flask provided with a column of bulbs to prevent loss of silver by spattering, in redistilled nitric acid diluted with an equal volume of water. After the silver was dissolved, the solution was diluted to twice its volume and was heated until free from nitrous fumes. Then it was still further diluted until not stronger than 1 per cent., and was slowly added, with constant stirring, to the 1 per cent. solution of cadmium bromide in the precipitating flask. In three analyses (4, 5 and 8), this procedure was varied by adding the bromide to the silver nitrate. After being shaken for some time, the solution was allowed to stand several days, with occasional shaking, until the supernatant liquid was clear. 30 cc. portions of the solution were then tested with hundredth normal solutions of silver nitrate and sodium bromide in the nephelometer[2] for excess of bromide or silver, and, if necessary, either standard silver nitrate or sodium bromide solution was

[1] Richards and Parker: Pr. Am. Acad. 32, 59.

[2] Richards and Wells: Am. Ch. J. 31, 235 (1904).

added, and the process of shaking and testing repeated, until the amounts of bromide and silver in the solution were equivalent. If the solution was perfectly clear when tested, and contained no considerable excess of bromide or silver, the test solutions were discarded, since they contained only negligible amounts of dissolved silver bromide; otherwise they were returned to the flask and a correction was applied for the silver bromide thus introduced.

As soon as the exact end-point of the titration had been found, about 4 centigrams of silver nitrate in excess were added, to precipitate dissolved silver bromide, and the flask was again shaken and allowed to stand until clear. The precipitate of silver bromide was collected upon a weighed Gooch crucible, after it had been washed by decantation about eight times with pure water. Then it was heated in an electric air-bath, first for several hours at 140°, finally for an hour at 200°, and, after it had cooled in a desiccator, it was weighed. In order to determine how much moisture was retained by the precipitate, in each case it was transferred as completely as possible to a clean porcelain crucible and weighed; then the salt was fused by heating the small covered crucible, contained in a large crucible, and again weighed. After fusion the silver bromide was light yellow, with only a trace of darkening, showing that no appreciable reduction had taken place. The asbestos mechanically detached from the Gooch crucible, together with a minute quantity of silver bromide which occasionally escaped the crucible, were collected from the filtrate and wash-waters upon a small filter, the ash of which was treated with nitric and hydrobromic acids before weighing. Although the filtrates and first wash-waters were essentially free from dissolved silver bromide, the subsequent wash-waters usually contained a trace of this substance. The amount of dissolved salt was determined with the nephelometer by comparison with standard bromide solutions. Finally, the weight of silver bromide was corrected for the sodium bromide introduced.

Although in our analyses of cadmium chloride no evidence could be obtained of appreciable occlusion of either cadmium or silver salts by silver chloride, especial precautions were taken to avoid any possibility of such a difficulty in this research. In the first place both the cadmium bromide and the silver nitrate

solutions were extremely dilute during precipitation, each one having a volume of about one liter. In the second place the method of precipitation was varied by sometimes adding the silver nitrate to the cadmium bromide (analyses 1, 2, 3, 6 and 7), and sometimes adding the bromide to the silver (analyses 4, 5 and 8). And in the third place the solutions were allowed to stand varying lengths of time before the titration was completed, so that occluded substances might have opportunity to be dissolved. Analysis 1, in which the largest quantity of bromide was employed, over 11 grams, which is to be expected to give the most marked evidences of occlusion, was not tested for five days after precipitation, and the titration was completed eight days later. In the other analyses the period between precipitation and the completion of the titration varied from seven days in analysis 4 to three days in analysis 8. Furthermore, in some cases, after the end-point had been reached, the solutions were allowed to stand some days longer with occasional testing. No change in end-point with standing was observed. In spite of these differences in the method of procedure, the variations in the final results do not exceed the experimental error to be expected, except in the case of analyses 4 and 12. Evidently, occlusion of any sort must have been very slight if it existed at all. Analyses 4 and 12, performed with the same bromide, differ so markedly from the others that, although no reason for the difference is known, they are rejected in computing the final average.

The gold-plated brass weights were carefully standardized to hundredths of a milligram. Vacuum corrections of +0.000090 for cadmium bromide,[1] of +0.000046 for silver bromide and of —0.000031 for silver were applied. All weighings were made by substitution with counterpoises as nearly like the objects to be weighed as possible. The atomic weight of silver is assumed to be 107.930 and that of bromine to be 79.955.

The analytical work was performed wholly by Mr. Hines.

The ratios of silver used to silver bromide obtained in the same analyses afford sufficient proof of the purity of the bromine and silver, as well as confirmatory evidence of the absence of appreciable occlusion by the silver bromide.

[1] The specific gravity of cadmium bromide has recently been found to be 5.192. Baxter and Hines: Am. Ch. J. 31, 220 (1904).

THE ATOMIC WEIGHT OF CADIMUM.

Ag = 107.930 Br = 79.955.

Series I. $CdBr_2$: 2Ag.

Number of analysis.	Sample of $CdBr_2$.	Weight of $CdBr_2$ in vacuum. Grams.	Weight of residue. Gram.	Loss in weight of boat. Gram.	Weight of Ag in vacuum. Grams.	Weight of Ag added or subtracted. Gram.	Corrected weight of $CdBr_2$. Grams.	Corrected weight of Ag. Grams.	Atomic weight of cadmium.
1	IIa	11.46220	0.00008	0.00004	9.08409	—0.00030	11.46216	9.08379	112.468
2	IIb	6.82294	0.00018	0.00006	5.40734	—0.00010	6.82282	5.40724	112.461
3	IIa	6.75435	0.00011	+0.00004	5.35297	—0.00020	6.75420	5.35277	112.465
4	IIIa	7.08590	0.00006	0.00004	5.61567	+0.00030	7.08588	5.61597	112.449
5	IIIa	5.13867	0.00008	0.00000	4.07236	—0.00010	5.13859	4.07226	112.473
6	IIIa	5.84328	0.00008	0.00004	4.63092	—0.00020	5.84324	4.63072	112.471
7	IIIa	5.99712	0.00008	0.00000	4.75269	—0.00010	5.99704	4.75259	112.472
8	IIa	5.90811	0.00017	0.00002	4.68200	0.00000	5.90796	4.68200	112.472
							Average rejecting analysis 4		112.470

Series II. $CdBr_2$: 2AgBr.

Number of analysis.	Sample of $CdBr_2$.	Weight of $CdBr_2$ in vacuum. Grams.	Weight of residue. Gram.	Loss in weight of boat. Gram.	Weight of AgBr. in vacuum. Grams.	Loss on fusion. Gram.	Weight of asbestos from filtrate. Gram.	Weight of AgBr from wash-waters. Gram.	Corrected weight of $CdBr_2$. Grams.	Corrected weight of AgBr. Grams.	Atomic weight of cadmium.
9	IIa	11.46220	0.00008	0.00004	15.81286	0.00024	0.00024	0.00033	11.46216	15.81319	112.466
10	IIb	6.82294	0.00018	0.00006	9.41251	0.00028	0.00044	0.00000	6.82282	9.41267	112.469
11	IIa	6.75435	0.00011	+0.00004	9.31815	0.00028	0.00043	0.00000	6.75420	9.31830	112.460
12	IIIa	7.08590	0.00006	0.00004	9.77557	0.00013	0.00053	0.00052	7.08588	9.77649	112.444
13	IIIa	5.13867	0.00008	0.00000	7.08897	0.00007	0.00043	0.00000	5.13859	7.08933	112.461
14	IIIa	5.84328	0.00008	0.00004	8.06076	0.00005	0.00033	0.00026	5.84324	8.06130	112.467
15	IIIa	5.99712	0.00008	0.00000	8.27321	0.00012	0.00020	0.00031	5.99704	8.27360	112.463
16	IIa	5.90811	0.00017	0.00002	8.15022	0.00015	0.00037	0.00026	5.90796	8.15070	112.463
									Average rejecting analysis 12.....		112.464
									Average of Series I and II, ...		112.467

	Ag : AgBr.
Analyses 1 and 9	57.4444
" 2 " 10	57.4464
" 3 " 11	57.4436
" 4 " 12	57.4436
" 5 " 13	57.4421
" 6 " 14	57.4438
" 7 " 15	57.4428
" 8 " 16	57.4429
Average,	57.4437

The most probable value for this ratio has been shown both by Stas and by experimenters in this laboratory to be 57.4445.[1]

In recent experiments in fusing manganous chloride, in a current of hydrochloric acid gas which had been dried by concentrated sulphuric acid and finally by means of phosphorus pentoxide, an insoluble residue of manganous phosphate was invariably obtained when the salt was dissolved in water. The quantity of this residue varied with the amount of moisture contained by the salt when brought in contact with the hydrochloric acid gas, being extremely slight if the salt was very nearly dry, but amounting to several milligrams if the salt still contained much of its crystal water. Although it seemed certain that the phosphorus had its origin in the phosphorus pentoxide, and was volatilized in the form of either phosphorus pentachloride or oxychloride through the action of the hydrochloric acid upon the pentoxide, in order to obtain still more positive evidence that this was really the case, the experiment was tried of passing hydrochloric acid gas which had been dried thoroughly by means of sulphuric acid, first over phosphorus pentoxide which had been freshly sublimed in a current of dry air, and then into water. The aqueous solution, upon evaporation and testing with ammonium molybdate gave a considerable amount of the characteristic ammonium phosphomolybdate. This result confirms that of Bailey and Fowler,[2] who have found that both hydrochloric and hydrobromic acids react with phosphorus pentoxide at ordinary temperatures to form the oxychloride and bromide of phosphorus respectively. The manganous phosphate, then, must have been produced by the action of the volatilized chloride of phosphorus

[1] Richards: Proc. Amer. Phil. Soc. 43, 119.

[2] Chem. News, 58, 22.

Average of Series I and II, ... 112.467

upon the moisture contained by the manganous chloride to form phosphoric acid, and subsequent displacement of hydrochloric acid from the salt by the phosphoric acid.

Although in our previous work with cadmium chloride, where the double cadmium ammonium chloride, $CdCl_2NH_4Cl$, was fused in a current of hydrochloric acid gas which had been finally dried with phosphorus pentoxide, the salt, which contains no crystal water, was essentially free from moisture before coming in contact with the hydrochloric acid, yet it seemed desirable to repeat the experiments with cadmium chloride in such a way that the danger mentioned above could be completely avoided. This result was easily attained by drying the hydrochloric acid gas with concentrated sulphuric acid only, four columns about 30 cm. in length, filled with beads moistened with sulphuric acid, being used for the purpose.

In order to ascertain whether concentrated sulphuric acid is appreciably attacked by hydrochloric acid gas, a large quantity of this gas was conducted through the columns and then into water. The aqueous solution was then evaporated and tested for sulphate with barium chloride. Although a slight precipitate of baric sulphate was produced, the quantity was estimated, by comparison in a nephelometer with a standard solution of a sulphate, to be less than five-hundredths of a milligram. Evidently nothing is to be feared from this source.

The material for these experiments was prepared from a portion of fraction II of cadmium sulphide, by first depositing the metal electrolytically from the sulphate as described above (page 771) and then dissolving the washed cadmium in pure hydrochloric acid in a platinum dish. The chloride does not lend itself readily to crystallization from aqueous solution on account of its great solubility even at low temperatures, but by conducting hydrochloric acid gas into the solution the much less soluble double salt with hydrochloric acid, $CdCl_2 2HCl 7H_2O$, was formed. The salt was thus crystallized three times with centrifugal drainage, to free it from the trace of sulphates occluded by the metal during electrolysis. Finally, it was dried and freed from hydrochloric acid as far as possible in a vacuum desiccator containing solid potassium hydroxide.

In analysis 18 the same specimen of silver was used as in analyses

4 to 8. In analyses 17 and 19 a new specimen which had been twice electrolyzed was employed.

The fusion, bottling and analysis of the salt were conducted exactly as described in the previous paper on cadmium chloride and also in this paper. A very slight insoluble residue in the cadmium chloride was determined as in the case of the bromide. The vacuum correction +0.000156 was applied to every apparent gram of cadmium chloride,[1] and of +0.000075 for every apparent gram of silver chloride. The analytical work was performed by Mr. Hines.

The average of these results is almost identical both with that obtained in the previous analysis of cadmium chloride, 112.469, and with that obtained from the bromide, 112.467, hence it is evident that no serious error was introduced in our earlier work by the use of phosphorus pentoxide for drying hydrochloric acid gas. Furthermore, in other analyses of chlorides in this laboratory, where the salts were fused in an atmosphere containing hydrochloric acid, either the salt employed was initially anhydrous, so that it could not have taken up the phosphorus, as in the case of magnesium ammonium chloride,[2] and of strontium chloride,[3] or else the concentrations of hydrochloric acid gas were so low that no error could have been introduced through the use of the hydrochloric acid, as in the case of calcium chloride.[4]

Although Bailey and Fowler attribute to hydrobromic acid an effect similar to that of hydrochloric acid, for several reasons it is certain that in the experiments upon cadmium bromide described in the earlier part of this paper no appreciable amount of phosphorus was introduced into the salt by the action of the hydrobromic acid upon the phosphorus pentoxide. In the first place, the experiment of passing into water hydrobromic acid gas, formed as in our work by passing nitrogen through bromine and then through an emulsion of red phosphorus in concentrated hydrobromic acid solution, and dried first by fused calcium bromide and then by phosphorus pentoxide, was performed in this laboratory some years ago in connection with the analysis

[1] The specific gravity of cadmium chloride has already been found to be 4.047. Baxter and Hines: Am. Ch. J., 31, 220 (1904).

[2] Richards and Parker: Pr. Am. Acad. 32, 55 (1896).

[3] Richards: Ibid. 40, 603 (1905).

[4] Richards: This Journal, 24, 374 (1902).

THE ATOMIC WEIGHT OF CADMIUM.

Ag = 107.930 Cl = 35.473[1]

$CdCl_2 : 2Ag$.

Number of analysis.	Weight of $CdCl_2$ in vacuum. Grams.	Weight of residue. Gram.	Loss in weight of boat. Gram.	Weight of Ag in vacuum. Grams.	Weight of Ag added or subtracted. Gram.	Corrected weight of $CdCl_2$. Grams.	Corrected weight of Ag. Grams.	Atomic weight of cadmium.
17	5.62511	0.00015	0.00004	6.61993	0.00000	5.62500	6.61193	112.472
18	6.81040	0.00026	0.00017	8.01516	0.00020	6.81031	8.01496	112.470
19	5.50097	0.00017	0.00009	6.47393	0.00000	5.50089	6.47393	112.470
							Average,	112.471

$CdCl_2 : 2AgCl$.

Number of analysis.	Weight of $CdCl_2$. in vacuum. Grams.	Weight of residue. Gram.	Loss in weight of boat. Gram.	Weight of AgCl in vacuum. Grams.	Loss on fusion. Gram.	Weight of asbestos from filtrate. Gram.	Weight of AgCl from wash-waters. Gram.	Corrected weight of $CdCl_2$. Grams.	Corrected weight of AgCl. Grams.	Atomic weight of cadmium.
20	6.11757	0.00004	+0.00003	9.56432	0.00013	0.00024	0.00147	6.11750	9.56590	112.470
21	6.81040	0.00026	0.00017	10.64731	0.00010	0.00061	0.00136	6.81031	10.64918	112.471
22	5.50097	0.00017	0.00009	8.59940	0.00008	0.00052	0.00190	5.50089	8.60174	112.469
								Average,		112.470

[1] Richards and Wells: Publications of the Carnegie Institution, No. 28, 1905; this Journal, 27, 459.

of cobalt and nickel bromides.[1] In this experiment no phosphorus could be discovered in the aqueous solution. In the second place, in two analyses of bromides which had been heated in hydrobromic acid gas, the filtrates from the silver bromide precipitates were evaporated to small bulk and tested for phosphoric acid, with negative results, while the slight residues obtained by filtering the aqueous solutions of the original bromides also showed in one case the complete absence of phosphorus, and in the other the presence of only a minute trace of this substance, although in the latter case the salt had been sublimed in a current of hydrobromic acid and therefore contained maximum amounts of phosphorus.[2] This result was to be expected from a consideration of the fact that the hydrobromic acid gas used in these experiments was diluted with at least twice its volume of nitrogen. In the light of this evidence it seems safe to assume that in the numerous analyses of bromides which have been carried out in this laboratory in recent years, no error was introduced by the use of phosphorus pentoxide as a drying agent for the hydrobromic acid gas. Nevertheless, with more concentrated hydrobromic acid, doubtless it would be unwise to use this drying agent.

It is interesting to compare the results of the analyses of the different fractions of material.

Fraction.			Average.
I.....	$CdCl_2 : 2Ag$	112.468	112.470
I.....	$CdCl_2 : 2AgCl$	112.471	
II, Series 1.....	$CdCl_2 : 2Ag$	112.456	112.469
II, Series 1.....	$CdCl_2 : 2AgCl$	112.481	
II, Series 2.....	$CdCl_2 : 2Ag$	112.471	112.471
II, Series 2.....	$CdCl_2 : 2AgCl$	112.470	
II.....	$CdBr_2 : 2Ag$	112.467	112.466
II.....	$CdBr_2 : 2AgBr$	112.465	
III.....	$CdBr_2 : 2Ag$	112.472	112.468
III.....	$CdBr_2 : 2AgBr$	112.464	
	Average.....	112.469	112.469

The close agreement of the results from fraction II by different methods and of the results from all three fractions leaves no doubt of the identity of the different specimens of material.

No matter how the results are averaged, the same conclusion

[1] Richards and Baxter: Pr. Am. Acad. 34, 361 (1899).

[2] Baxter: Pr. Am. Acad. 39, 248 (1903).

is reached as in the preliminary paper, *i. e.*, that the atomic weight of cadmium lies very near the value 112.47 (Ag = 107.930).

It is interesting to compare the results of our work with those obtained by other experimenters. From the following list[1] of

[1] The greater portion of this list is to be found in Clarke's "Recalculation of the Atomic Weights," Smithsonian Misc. Coll. 1897.

Stromeyer: Schweigger's Jour. **22**, 366 (1818).

Cd : CdO	111.5
Cd : CdS	113.8
Cd : Cl_2	112.8
Cd : I_2	111.7

von Hauer: J. pr. Chem. **72**, 350 (1857).

$CdSO_4$: CdS	111.94

Lenssen: J. pr. Chem. **79**, 281 (1860).

CdC_2O_4 : CdO	112.0

Dumas: Ann. Chem. Pharm. **113**, 27 (1860).

$CdCl_2$: 2Ag	112.43
	111.95

Huntington: Pr. Am. Acad. **17**, 28 (1881).

$CdBr_2$: 2Ag	112.24
$CdBr_2$: 2AgBr	112.23

Partridge: Am. J. Sci. (3) **40**, 377 (1890).

CdC_2O_4 : CdO	111.80
$CdSO_4$: CdS	111.73
CdC_2O_4 : CdS	111.67

Morse and Jones: Am. Ch. J. **14**, 261 (1891).

Cd : CdO	112.07
CdC_2O_4 : CdO	112.02

Lorimer and Smith: Z. anorg. Chem. **1**, 364 (1892).

CdO : Cd	112.04

Bucher: Doctoral Dissertation, Baltimore, Md. (1895).

CdC_2O_4 : CdO	111.88
CdC_2O_4 : CdS	112.15
$CdCl_2$: 2AgCl	112.37
$CdBr_2$: 2AgBr	112.39
Cd : $CdSO_4$	112.35
Cd : CdO (porcelain)	112.08
Cd : CdO (platinum)	111.89

Hardin: This Journal, **18**, 1016 (1896).

$CdCl_2$: Cd	112.12
$CdBr_2$: Cd	112.06
Cd : Ag	111.99

Morse and Arbuckle: Am. Ch. J. **20**, 536 (1898).

Cd : CdO	112.38

Baxter and Hines: This Journal, **27**, 222 (1905).

$CdCl_2$: 2Ag	112.462
$CdCl_2$: 2AgCl	112.476

investigations upon the atomic weight of cadmium it can be seen that this subject has attracted considerable attention, especially in recent years. The following atomic weights are assumed: O = 16.00; C = 12.00; S = 32.06; Cl = 35.47; Br = 79.96; Ag = 107.93; I = 126.98.

The relative value of many of these determinations has already been several times discussed,[1] and since it is invariably a difficult matter intelligently to criticize experimental work without an actual repetition of the experiments, for frequently some constant source of error is so securely hidden that it may be detected only by the most careful investigation, no attempt at criticism is made here.

Furthermore the uncertainty which now exists as to the relation between several fundamental atomic weights, *e. g.*, silver and oxygen,[2] makes it a matter of considerable doubt whether, when this uncertainty is removed, some of the discrepancies in the foregoing table will not disappear.

Attention should be called to the agreement with ours of the results of Bucher's painstaking work upon the halogen compounds of cadmium. The values from cadmium chloride vary between 112.26 and 112.46, with an average of 112.37, but if the first seven of his twenty-one experiments are rejected, his average becomes 112.40, and six of his results are as high as 112.43. His analyses of the bromide vary between 112.30 and 112.46, with an average of 112.39.

The results of this investigation are then as follows:

(1) The value for the atomic weight of cadmium previously found by analysis of cadmium chloride, 112.47 (Ag = 107.930), is supported by the analysis of cadmium bromide and by new analyses of cadmium chloride.

(2) Phosphorus pentoxide is found to be attacked by pure hydrochloric acid gas, and hence is unsuited for drying this gas, thus confirming the results of Bailey and Fowler.

[1] Clarke, Partridge, Morse and Jones: Loc. cit.; Richards: Am. Ch. J. 20, 547 (1898).

[2] Richards: Publications of the Carnegie Institution, No. 28, page 67; Report of the International Committee on Atomic Weights, This Journal, 28, 1 (1906).

(3) It is shown that no appreciable error is introduced from this source, if a *dry* salt is fused in a current of hydrochloric acid which has been dried by phosphorus pentoxide.

(4) It is pointed out that in the case of hydrobromic acid diluted with twice its volume of nitrogen no similar effect is produced.

We are deeply indebted to the Carnegie Institution of Washington with whose generous aid this investigation has been completed, and also to the Cyrus M. Warren Fund for Research in Harvard University for indispensable platinum vessels.

CHEMICAL LABORATORY OF HARVARD COLLEGE,
CAMBRIDGE, MASS., U. S. A.,
March 29, 1906.

ON THE CHEMICAL ACTION OF ULTRA-VIOLET LIGHT.

BY W. H. ROSS.

Received January 18, 1906.

THE work herein described was undertaken with a view to making especially some quantitative measurements on the chemical action of light. Since in the majority of chemical changes the greatest effect is produced by ultra-violet light, it was thought advisable to work with a source of light rich in these rays. Such a source was obtained by causing an oscillatory spark to pass between aluminium terminals joined in the secondary circuit of a large induction coil used as a transformer. In the secondary circuit was also joined in parallel a large Leyden jar. Through the primary circuit was passed an alternating current of 110 volts having a strength of 3.4 amperes. To obtain a constant source of light proved a matter of considerable difficulty. However, by arranging an apparatus as thus described and having in the primary circuit an ammeter and resistance boxes, the resistance could be changed at will and the strength of the current thus kept constant. When a uniform current was in this way maintained, the amount of energy given out by the spark during intervals of ten minutes was practically constant. This was shown to be the case by the fact that the same amount of iodine was set free from equal volumes of a potassium iodide solution, when exposed to the light under exactly the same conditions for equal intervals of time. After every observation the aluminium terminals were sharpened, and then placed the same distance

apart so that every exposure might be begun under the same conditions. The terminals used were large—3 mm. by 8 mm. cross-section—and were allowed to rest for the greater part of their length on iron plates placed 7 cm. apart. In this way the heat generated by the spark was rapidly conducted away. By placing the proper amount of ice in small dishes resting on the terminals, the temperature of a solution of 3 cc., placed in a cell directly underneath the spark, could be kept within a range of 1° during an exposure of ten minutes.

Aluminium terminals were used on account of the strong ultra-violet rays given out by a spark passing between them. The rate of decomposition produced by the light in the case of the iodides, when terminals of aluminium were used, was found to be at least twice as great as that resulting when terminals of any of the other common metals were used. Cadmium could not be used on account of its softness. An accurate comparison of the decompositions produced, when electrodes of different metals were used, was not made, since, on account of their difference in hardness, the experiments could not be carried out under comparable conditions.

DECOMPOSITION OF THE IODIDES.

The compounds first investigated were the iodides of the different metals in solution. The solution to be exposed to the light was placed in a shallow vessel directly underneath the spark. The amount of iodine set free was determined by titrating with a standard solution of sodium thiosulphate, using starch as indicator. When making exposures of ten minutes, the most convenient strength of the sodium thiosulphate was found to be 1/1000 normal. With a solution of this strength the amount of iodine set free could not be determined by titrating with the thiosulphate directly. By adding an excess of the thiosulphate solution, however, and then titrating with a 1/1000 normal solution of iodine, the amount of iodine set free could be accurately determined.

It was noticed when making titrations that the purest water obtainable, that used in this laboratory for making electrical conductivity measurements, had the power of decolorizing quite an appreciable amount of iodine. Thus, to 20 cc. of water, containing a few drops of starch solution, had to be added from

0.2 cc. to 0.4 cc. of a 1/1000 normal solution of iodine before any blue color appeared. With an iodide present a less amount of the iodine solution was required. Hence, before titrating any solution exposed to the light, a blank titration of a solution containing the same amount of iodide, was made in every case in order that the proper correction to be applied might be found.

When a solution of potassium iodide was exposed to the light in an open vessel, the amounts of iodine set free, on making exposures for equal intervals of time, varied greatly. When the distance of the solution from the spark was doubled, the rate of decomposition remained almost the same as before. The spark was then made to pass through an atmosphere of oxygen. This was done by placing the terminals in a large bell-jar filled with the gas. Under these conditions, the rate of decomposition was found to be very much increased. In replacing the oxygen with carbon dioxide, the amount of decomposition resulting in the same length of time was very small. It therefore became evident that the greater part of the decomposition first obtained was produced, not by the light only, but principally by the action of ozone and the oxides of nitrogen formed by the passage of the spark through air.

To determine the effect of the ultra-violet light only, the solution was placed in a small shallow dish provided with a quartz cover. The latter was sealed into a rim of hard rubber which was in turn surrounded by an elastic rubber band. This then could be slipped over the top of the dish so as to secure the complete exclusion of any gas. When the dish was now placed underneath the spark, the decomposition resulting represented the total effect of the waves of light given out by the spark. By subtracting from this the effect produced when a thick piece of glass plate was interposed between the spark and the solution, the effect of the ultra-violet light alone, or that part of it capable of being absorbed by the glass, was determined. When a photograph of the spectrum given by the spark was taken by means of a spectroscope, it was found that, when the glass plate used in the following experiments was interposed between the spark and the spectroscope, all wave-lengths were absorbed below λ 3260.

That the decomposition of the iodide, which took place when gases formed by the spark were excluded, was due to the action of the light alone was shown by varying the distance of the solu-

tion from the spark. It was now found that the amount of iodine set free varied inversely as the square of the distance, which one would expect if the decomposition is due entirely to the amount of light energy incident upon the solution. When making exposures, 3 cc. of the solution were taken in every case, while the time of exposure was ten minutes.

The effect produced on solutions of potassium iodide of different concentrations is shown in the following table:

Gram mol. KI per liter.	I set free measured in cc. of $N/_{1000}$ solution.	Gram mol. KI per liter.	I set free measured in cc. of $N/_{1000}$ solution.
3.0	3.58	0.05	1.50
2.0	3.35	0.02	1.15
1.0	3.00	0.01	1.00
0.5	2.68	0.005	0.80
0.2	2.15	0.002	0.50
0.1	1.85	0.001	0.40

Duplicate observations, which agreed with one another within 0.1 cc., were made in every case.

On varying the time of exposure, the amount of iodine set free was not at first exactly proportional to the time. This agrees with what might be expected for the color of the solution, or its power of absorption, changes after a short exposure. A tenth-normal solution was used in each case.

Time of exposure.	I set free in cc. of $N/_{1000}$ solution.
10	1.85
20	3.30
30	4.90

When making these observations, the terminals were sharpened and placed the same distance apart every ten minutes.

When the glass plate already referred to was interposed between the spark and the solution, the amount of iodine set free was very small. Thus, in the case of a twice normal solution of potassium iodide, the amount set free was found to be equivalent to only 0.15 cc. of a 1/1000 normal solution of iodine, while in the case of a 1/10 normal solution no free iodine could be detected after an exposure of ten minutes. When working with the more concentrated solution, the amount of iodine set free by the action of the visible light was subtracted from the total amount set free to get the results given above.

The iodides of sodium, lithium, barium, calcium and zinc were

next investigated, but all were found to give the same results as those given by potassium iodide.

Gram equivalents of iodide per liter.	Iodine set free in cc. of $N/_{1000}$ solution.					
	KI.	NaI.	LiI.	BaI_2.	CaI_2.	ZnI_2.
2.0	3.35	3.40	3.35	3.45	3.37	3.40
0.5	2.68	2.60	2.65	2.70	2.73	2.70
0.1	1.85	1.80	1.85	1.75	1.80	1.85
0.01	1.00	1.00	1.05	1.00	1.03	1.00

These observations were made at a temperature of 18°. A variation, however, in the temperature of any of the solutions between 15° and 30° produced no appreciable change in the rate of decomposition.

REDUCTION OF FERRIC SALTS.

Solutions of the sulphate, nitrate and chloride were standardized by reducing with stannous chloride and then titrating with potassium permanganate in the presence of manganese sulphate and phosphoric acid. That the solutions thus standardized as regards the iron also contained equivalent amounts of acid, was shown by titrating a definite portion of each solution with a standard sodium hydroxide solution, using phenolphthalein as indicator.

When two Nessler tubes surrounded with white paper were filled with the standard sulphate and chloride solution, it was noticed that the first solution was slightly darker than the second, but on adding to it a few drops of acid it could be brought to the same color as the other when thus viewed by reflected light. When the tubes with the paper coverings removed were placed so as to view the solutions by transmitted light, the sulphate solution was now much lighter in color than the chloride solution. This shows that the two solutions have a different power of absorption for light. Hence, when acted upon by light of the same intensity, it was found, as might be expected for this reason alone, that the solutions were not reduced at the same rate.

As is well-known, the action of light on ferric salts is very much increased when there is present in solution some organic compound as cane-sugar, which of itself will not reduce the salts but does so under the influence of light. Hence, when working with these solutions a definite amount of sugar was always added.

The amount of salt reduced was determined by titrating with a

standard 3/400 normal solution of potassium permanganate. When finding the effect of ultra-violet light on solutions of different strength, a 1/5 normal solution was first taken to which was added 10 grams of sugar per 50 cc. of solution. A 1/10 normal solution was then prepared by adding to a definite volume of the 1/5 normal solution an equal volume of water. Solutions of other dilution were prepared from the 1/5 normal solution in the same way.

With ferric chloride, sulphate and nitrate the following results were obtained on making exposures of ten minutes:

Gram-equivalents. of salt per liter.	Ferrous salt formed in cc. of $3N/_{400}$ solution. $FeCl_2$.	$FeSO_3$.	$Fe(NO_3)_2$.
0.20	2.50	2.45	0 55
0.10	2.25	1.70	0.50
0.05	1.93	1.05	0.48
0.02	1.27	0.50	..
0.01	0.85	0.40	..
0.005	0.70	..	..
0.002	0.60	..	..

The amount of sugar added has a considerable effect on the amount of reduction which takes place as is shown thus:

Percentage of sugar added.	$FeCl_2$ formed in cc. of $3N/_{400}$ solution.
10	1.73
20	2.50
40	3.22

The amount of ferric salt reduced is approximately proportional to the time of exposure. A 1/5 normal solution of ferric chloride containing 10 grams of sugar per 50 cc. of solution gave results as follows:

Time of exposure.	$FeCl_2$ formed in cc. of $3N/_{400}$ solution.
10 minutes	2.53
20 minutes	4.70
30 minutes	7.15

Varying the temperature of any ferric salt solution was found to have a slight effect on the rate of reduction.

REDUCTION OF CHLORATES AND BROMATES.

While solutions of the chlorates and bromates are quite stable in sunlight, they were found to be reduced to quite an extent when acted upon by that part of the ultra-violet spectrum capable of being absorbed by glass. The extent of the reduction was deter-

mined by titrating the amount of chloride or bromide formed by means of a 1/200 normal solution of silver nitrate. It was found that solutions of all chlorates of the same strength were reduced at the same rate, while the same thing was true of the bromates. The rate of reduction of the chlorates, however, differed from that of the bromates. Unlike the iodides or ferric salts, varying the strength of either the chlorate or bromate solutions from 1/2 to to 1/50 normal did not produce any appreciable difference in the amount of reduction which took place.

Gram-equivalents of $KClO_3$ [or $NaClO_3$, $Ba(ClO_3)_2$, etc.] per liter.	Chloride formed in cc. of $N/_{200}$ solution.
0.50	0.80
0.10	0.80
0.02	0.80
0.01	0.78

In the case of the bromates the amount of salt reduced was less than in the case of the chlorates. Thus, when the strength of any standard bromate solution was varied from 1/2 to 1/100 normal, the amount of bromide formed in every case was equivalent to only 0.25 cc. of a 1/200 normal silver nitrate solution.

The amount of chlorate or bromate reduced was found to be exactly proportional to time of exposure.

Sugar added to solutions of the chlorates or bromates resulted in an increase in the amount of reduction which took place, but to a much less extent than in the case of the iron salts. Varying the strength of the solution now produced a change in the amount of reduction. A 1/2 normal solution of potassium chlorate containing 10 grams of sugar per 50 cc. of solution, when diluted so as to make a 1/20 normal solution, gave the same results, however, as one containing no sugar.

Gram mol. of $KClO_3$ per liter.	Chloride formed in cc. of $N/_{200}$ solution.
0.5	1.50
0.2	1.15
0.1	0.90
0.05	0.80
0.01	0.80

When sugar was added to the bromate solutions, a greater amount of reduction took place than in the case of the chlorates.

Gram mol. of bromate per liter.	Bromide formed in cc. of N/200 solution from $KBrO_3$.	$NaBrO_3$.	$Ba(BrO_3)_2$.
0.5	1.75	1.73	1.75
0.2	1.55	1.50	1.55
0.1	1.40	1.42	1.37
0.05	1.20	1.20	1.25

Before making a titration to determine the amount of change produced in any particular solution, a blank titration was first made in every case.

I wish to express my thanks to Professors Jones and Wood at whose suggestion this work was undertaken.

JOHNS HOPKINS UNIVERSITY,
BALTIMORE, MD.

A GAS GENERATOR FOR HYDROGEN SULPHIDE, HYDROGEN AND OTHER GASES.

BY ALLEN P. FORD.

Received March 27, 1906.

THE principle of the generator shown in the accompanying sketch is by no means new. The general form of the present apparatus was shown and described[1] by H. G. Schanche. An improved form was described[2] by Augustus E. Knorr, the improvement consisting essentially of a siphon tube which allowed automatic escape of the exhausted acid.

A generator was made in our laboratory after the plan of this improved one, which worked well, but it was found that the water in the wash-bottle would suck back into the calcium chloride jar over night, owing to the absorption of the gas and the consequent creation of a partial vacuum. This, together with the fact that it sometimes did not start up readily after lying idle some time, owing to the accumulation of sediment and crystallized salts, gave considerable annoyance, and the result of the experience and consequent experimenting is the form of apparatus shown herewith.

It needs no detailed description as the cut is self-explanatory. The apparatus is self-sustaining, all being carried on one base with the exception of the small wash-bottle. The automatic overflow for the spent acid is out of the way, a small hole in the

[1] This Journal, **16**, 868 (1894).

[2] Ibid. **19**, 818 (1897).

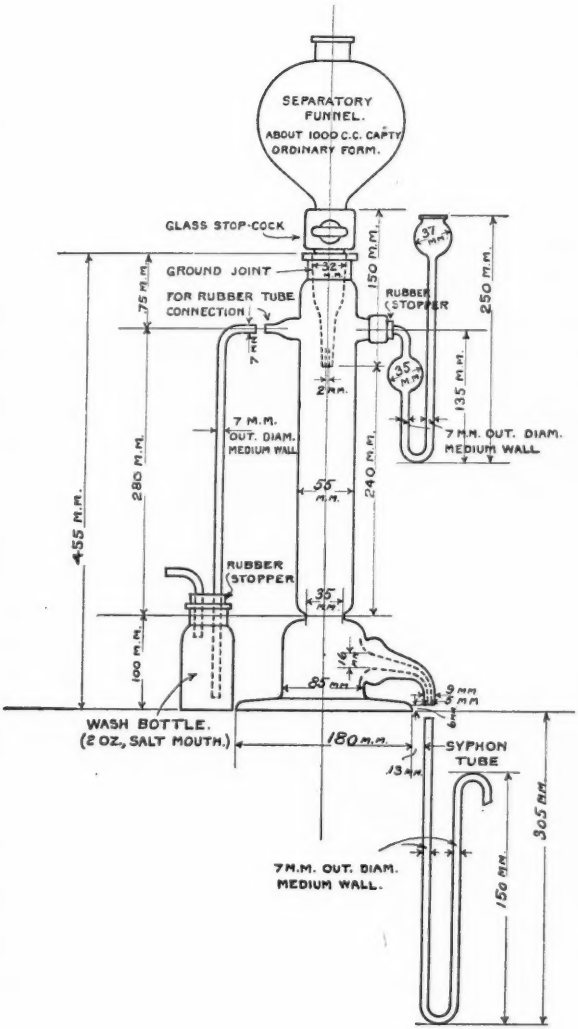

SEPARATORY FUNNEL.
ABOUT 1000 C.C. CAPTY.
ORDINARY FORM.
GLASS STOP-COCK
GROUND JOINT
FOR RUBBER TUBE CONNECTION
RUBBER STOPPER
RUBBER STOPPER
7 M.M. OUT. DIAM. MEDIUM WALL.
7 M.M. OUT. DIAM. MEDIUM WALL.
7 M.M. OUT. DIAM. MEDIUM WALL.
WASH BOTTLE. (2 OZ., SALT MOUTH.)
SYPHON TUBE
75 M.M.
280 M.M.
455 M.M.
100 M.M.
150 M.M.
240 M.M.
250 M.M.
135 M.M.
55 M.M.
180 M.M.
305 MM.
150 MM.
85 MM.
13 MM.
2 MM.
9 MM.
5 MM.
32 M.M.
35 M.M.
37 MM.

table top allowing the siphon tube to be carried underneath, whence it can discharge into any convenient receptacle.

The safety tube connected to the side of the calcium chloride jar opposite the gas outlet is the new feature, and this prevents the water in the wash-bottle from being drawn back, and also allows the apparatus to be washed out and cleaned of any sediment or incrustation of salts, by simply pouring a beaker of water through it.

This apparatus[1] is not particularly recommended for a qualitative class room or similar place where small quantities of hydrogen sulphide are required repeatedly and instantly by turning on the stop-cock, but for a laboratory where a steady flow of gas is required for longer or shorter periods, where the flow must be uniform and where the generator is required to be always in commission whether used every day or once a month, it will be found highly satisfactory.

Since our first home-made one upon which the experimenting was done, we have had three made to order, one in this country and two in Germany. They are well made, sightly pieces of apparatus, and take up very little room.

The calcium, chloride jar will hold three or four pounds of iron sulphide or zinc in broken pieces, and until it needs replenishing the generator will require no attention, whether used much or little, except the occasional filling of the acid reservoir and a possible washing by running some water through it by means of the safety tube. At no time is it necessary to break a joint or take the generator apart in any way, except when recharging with iron sulphide, and even this is very easily done.

It is as easily and quickly started after standing a month as after standing a day, and altogether we have found it the most satisfactory gas generator we have ever used.

THE EATON, COLE AND BURNHAM CO.,
BRIDGEPORT, CONN.

[1] It may hardly be necessary to state that the accuracy of most of the measurements in the drawing are not important, but were taken from a generator in actual use to make the drawing plain. In two or three places, however, these figures should be rather carefully followed, for instance, the distance from the glass stop-cock in the separatory funnel to the outlet of same should not be less than five or six inches, else when the funnel is nearly empty the column of liquid might not be equal to that through which the gas was being forced, with the result that it would escape through the acid in the

NOTE.

A New Synthesis of Ethyl Methyl Xanthic Ester.—The fact has been pointed out that metallic magnesium and methyl alcohol do not react under the ordinary conditions of temperature and pressure, but upon the addition of a small particle of iodine, or a few drops of a nitro-compound, reaction begins, hydrogen is evolved and the methylate of magnesium is formed.[1] Certain alkyl halides and even carbon bisulphide induce the reaction between magnesium and methyl alcohol.

It is the reaction between carbon bisulphide, methyl alcohol and magnesium that is now to be considered. While making preliminary tests a marked difference in the appearance of the reaction-product was noticed according as magnesium was allowed to react with a dilute or a concentrated solution of carbon bisulphide in methyl alcohol. In the case of the dilute solution the reaction-product was light yellow in color and very thickly gelatinous, this latter property being due to the supposed formation of magnesium methylate. On the other hand, where carbon disulphide was present in excess, no precipitate was formed and the solution was of a deep blood-red color.

These observations led to the conclusion that when magnesium reacts with a solution of carbon bisulphide in methyl alcohol, magnesium methylate tends to form, and this then in turn, in the presence of an excess of carbon bisulphide, reacts to form magnesium methyl xanthate.

These reactions may be represented as follows:

$$Mg + 2CH_3OH = Mg(OCH_3)_2 + H_2.$$

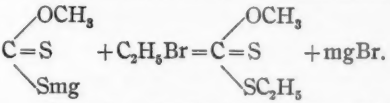
$$C\begin{matrix}S\\S\end{matrix} + mgOCH_3 = C\begin{matrix}OCH_3\\Smg^2\end{matrix}=S \quad .$$

funnel. Again, the outlet opening of the separatory funnel should not be more than 2 or 3 mm. in diameter to prevent the stem from emptying when the stop-cock is turned off. Also, the form and size of the outlet tube at the bottom of the calcium chloride jar should pretty closely approximate the drawing to assist the used acid in running off without filling the tube until it reaches the perpendicular part. The importance of this point is not so apparent until one has experimented with it.

[1] H. S. Fry: This Journal, "Action of Magnesium upon Methyl Alcohol" (yet to be published).

[2] mg = ½ Mg.

Now if magnesium methyl xanthate is thus formed it should in turn react with an alkyl halide, such as ethyl bromide, to form an ester of the hypothetical methyl xanthic acid, namely, ethyl methyl xanthic ester, in accordance with the following reaction:



That such reactions do actually take place with the final production of ethyl methyl xanthic ester is evident from the following experimental part.

Experimental Part.—One-half of a gram-molecule (12 grams) of magnesium, 152 grams of carbon bisulphide (twice the theoretical amount in order to insure an excess), and 500 cc. of methyl alcohol were placed in a 2-liter round-bottomed flask equipped with a long reflux condenser. The reaction began immediately and proceeded with increasing energy so that in the course of about ten minutes the contents of the flask were boiling violently. Five minutes later all of the magnesium had disappeared, and the resulting reaction mixture, which was of a clear deep red-brown color was heated to boiling upon the water-bath for two hours in order to effect complete reaction between the carbon bisulphide and any magnesium methylate that was in solution.

After the contents of the flask had cooled down to the room temperature, 120 grams of ethyl bromide were added. This amount was a slight excess over that actually required to combine with the magnesium as methyl xanthate. As soon as the ethyl bromide was added the contents of the flask became warmer, and in the course of a few minutes were boiling actively. The color of the solution rapidly changed from deep red brown to pale yellow. The reaction mixture was again boiled for two hours to insure complete reaction between the ethyl bromide and the magnesium methyl xanthate.

In order to obtain the ethyl methyl xanthic ester thus formed, a liter of water slightly acidified with sulphuric acid was added to the reaction mixture in the flask. A heavy yellow oil separated out and was extracted with ether in a separatory funnel. The ether solution thus obtained, after being neutralized, washed with water and filtered, was subjected to distillation.

By distillation at boiling-water-bath temperature the ester was freed from ether, carbon bisulphide, ethyl bromide, and methyl alcohol. Further distillation with a direct flame yielded 85 grams of a light yellow oil, distilling at 184° C., the boiling-point of ethyl methyl xanthic ester. The yield was 62.50 per cent. of the theoretical.

Further distillation to 200° C. resulted in the decomposition of the residue in the distilling flask, a very small quantity of distillate passing over.

This synthesis affords an example of the analogy between magnesium and sodium or potassium methylates which later are commonly used in the preparation of various xanthic esters in accordance with analogous reactions. H. S. FRY.

UNIVERSITY OF CINCINNATI.

NEW BOOKS.

URIC ACID. THE CHEMISTRY, PHYSIOLOGY AND PATHOLOGY OF URIC ACID AND THE PHYSIOLOGICALLY IMPORTANT PURIN BODIES WITH A DISCUSSION OF METABOLISM IN GOUT. By FRANCIS H. MCCRUDDEN. New York: Paul B. Hoeber. 1905. 318 pages. Paper: $2.50; Canvas, $3.00 net.

In the main this work is a compilation of the important scientific literature on the subject of uric acid in the several relations indicated by the title; these relations are discussed in separate sections and the various sub-topics are so chosen as to practically cover the whole field.

In the preface the author explains the motives which led him to make this extensive compilation. He refers especially to the views held by Haig on the great importance of uric acid in bringing about certain pathological conditions, which views were everywhere treated with a degree of consideration entirely out of proportion to the value of the experiments and observations on which they were based. Few subjects have received more attention from medical writers than has uric acid as a factor in the causation of disease, and the advertising columns of the medical journals and the daily press shown that advantage has been taken of this by enterprising manufacturers in turning out a host of remedies, mostly frauds, for the treatment of the so-called "uric acid diathesis." In no field of medicine is there greater humbug.

McCrudden has undertaken to determine by a thorough study of the literature just what is accurately known of the conditions of formation and excretion of uric acid in the animal body. As a man quite familiar with the subject from his previous studies and experimental investigation he has done his work well. The literature references given appear to be very complete, and the book must have a distinct value for the physiological chemist or pathologist interested in this line of research. All the recent chemical work bearing on the relations of the purines is fully considered, which adds much to the practical usefulness of the book for reference. A consideration of all the data presented is sufficient to thoroughly dispose of the Haig and similar doctrines.

J. H. LONG.

THE PENNSYLVANIA RAILROAD SYSTEM AT THE LOUISIANA PURCHASE EXPOSITION. LOCOMOTIVE TESTS AND EXHIBITS. St. Louis, Missouri, 1904. First edition. Philadelphia: The Pennsylvania Railroad Company.

The introduction to this most important document opens with the following statement: "The exhibit of the Pennsylvania Railroad System at the Louisiana Purchase Exposition was designed primarily to show the application of Civil and Mechanical Engineering to the needs of a large railroad." Certainly the report shows that the purpose of the exhibit was fully and completely carried out as would naturally be expected of the system.

As an example of mechanical engineering the locomotive testing plant was presented. The idea of the system of testing as here carried out is credited to Alexander Bowdin of Russia, but the credit of its practical application is given to Professor Goss of Purdue University who seems to have been the first to support a "running locomotive on wheels" and in a laboratory where conditions could be kept constant and without the interruption and variations common in road tests.

In preparing the exhibit and making the tests other railroads were invited to send locomotives and representatives of their engineering forces to aid in testing all the locomotives.

It is stated that "the Pennsylvania Railroad System brought into existence an entirely new testing plant for mounting either freight or passenger locomotives and capable of absorbing for an indefinite period the maximum power of a modern locomotive

when running at any rate of speed between 10 and 75 miles per hour;

"It caused to be designed and constructed a dynamometer capable of registering the tractive power of the heaviest locomotive and at the same time so sensitive as to indicate the slightest variation of force it may exert."

"It has purchased and standardized instruments and apparatus for use in securing all data which have been deemed to be of scientific interest;

"It has organized a complete corps of observers, engineers and computers to carry out the tests and to record, tabulate and analyze the results;

"It has invited and secured the coöperation of scientific and technical men of this and other countries to assist in placing the tests upon the highest plane possible in such work;

"It has overcome difficulties in many cases perplexing and serious, incident to carrying out of such work as a part of a great International Exposition;

"It has as a result of its effort defined the action of eight different typical locomotives as regards performance of the boiler, the engine and the locomotive as a whole under many different conditions of operation making of record a mass of information concerning the economic performance of the modern locomotive of great immediate value and supplying a basis of comparison which will prove useful for many years to come;

"It has met the expenses of equipping and operating the plant with instructed hand, always holding considerations of cost subordinate to the definite object of making the tests as complete and valuable as possible, notwithstanding the fact that the amounts involved have been greater than have ever been appropriated to any similar undertaking;

"It has undertaken a broad plan of publication which is to result in making all its data derived from the tests, and all conclusions based thereon, together with a description of all methods and means employed, all in great detail, accessible to railroad officials and locomotive designers throughout the world."

Special credit is awarded by the Advisory Committee to Messrs. J. J. Turner, Third Vice-president, Theo. N. Ely, Chief of Motive Power, F. D. Casanoor, W. A. Gibbs, A. S. Vogt, E. D. Nelson and G. L. Wall.

We have reproduced here this part of the introduction to their report by the Advisory Committee because it must interest men in every learned profession to have knowledge of work of this class carried out in connection with an International Exposition, illustrating fully and well what the work of such an exposition should be, truly a faithful record of the world's progress in the arts and industries, made in such a way as to be of use for all time. Such work has been attempted in other lines and in other expositions, but never on such a scale an dwith such practical and accurate results. The results published in this report are of universally greater interest to the mechanical engineer than to the working chemist but even to the latter class they are far from being without value, and many chemists in charge of works will be interested in the volume of data regarding the relation between fuel consumption and steam production and will be interested to learn that in the best types of locomotive boilers in these tests the weight of water evaporated per pound of coal consumed—water from and at 212° F.—varied from 5.5 to 12.5 pounds. Some of us will find comfort in these figures and relief from discouragement which has followed similar tests in the boiler plants of the works, to which the closest attention practicable has been given.

The volumes of results of analysis of fuels used in the tests are of interest and value as are the analyses of the smoke gases, while the methods of analysis will remain the standard for such work. The analyses of coals were made in accordance with the method decided on by the Committee of the American Chemical Society and given in Vol. 21, No. 12, of this Journal. Analyses were made of coal, sparks and ash. Altogether the work will be accepted as high authority by mechanical engineers and will, in very many ways, prove useful to working chemists as well.

The Pennsylvania Railroad System deserves the thanks of the scientific world for having carried out this splendid work and congratulations upon the splendid results obtained.

W. McMURTRIE.

THE UNITED-OTTO SYSTEM OF BY-PRODUCT COKE OVENS. United Coke and Gas Company, New York City, 1906.

As appears from the well-known compilations prepared by Dr. Edward W. Parker, and from Mr. John Fulton's standard treatise on coke, it was only about thirteen years ago that the first

plant of by-product coke ovens was erected in the United States. This plant was of the type known as Semet-Solvay ovens, and was installed at Syracuse, N. Y., in connection with the works of The Solvay Process Company. During the comparatively brief period that has since elapsed, the total number of by-product coke ovens constructed in the United States by the Semet-Solvay Company and the United Coke & Gas Company has risen to a total in excess of 3,000, which in 1904 produced about 11 per cent. of all the coke made in the entire country.

Among the plants thus far constructed are the Semet-Solvay ovens in Pennsylvania, West Virginia, Alabama, and elsewhere, for the Pennsylvania Steel Company, Tennessee Coal, Iron & Railway Company, National Tube Company, and others, while the United Coke & Gas Company has erected plants of the type known as the United-Otto ovens, for the Cambria Steel Company, Lackawanna Steel Company and Sharon Coke Company, in Pennsylvania, and for other concerns elsewhere, and the increase in the number of by-product ovens is being continued by the plant just completed by the Semet-Solvay Company at Chicago, which is about to be further enlarged; its new plant under construction at Steelton, Pa., for the Pennsylvania Steel Company, and the additions under way or recently completed at the United-Otto plants at Cambria, Pa., and Camden, N. J.

As is familiarly known, the chief advantages offered by the by-product oven over the old-fashioned type known as the "bee-hive," consist in the production of a larger percentage of coke, of equally high quality, and the saving of large quantities of gas in excess of that used for heating the ovens, together with tar and ammonia, and certain derived products. These advantages are discussed in an instructive and entertaining manner, from the point of view of the United Coke & Gas Company, in a very handsome and attractive volume recently issued by it. To the careful reader it will probably appear, however, that the claims there set forth are somewhat more optimistic than the actual facts may warrant. In many localities, for example, the market for fuel or illuminating gas is already fully supplied, and the total output of tar in the United States is now in excess of the demand. On the basis of an output of 9 gallons of tar per ton of coal carbonized, a moderate sized plant carbonizing say 1,000 tons of coal per day, would add to the present production of tar a further amount in

excess of three and one-quarter million gallons of tar per annum. And on the basis of an output of 5 pounds of ammonia (NH_3), equivalent to say 20 pounds figured as ammonium sulphate, per ton of coal carbonized, the same plant would add to the present production a further amount in excess of seven million pounds of sulphate per annum, so that any general and sudden increase in the number of by-product coke ovens would apparently result in depriving that type of construction, not only in the new plants but also in those previously erected, of the greater part if not all of the advantages resulting from its output of by-products, for these plants themselves involve a much larger initial investment, and thereafter cost more to operate, than those of the bee-hive type, the returns from the by-products being relied on, with the increased yield of coke, to cover these extra charges and show some net gain in the final result. In other words, it seems entirely probable that it is only in proportion to the gradual enlargement of the field in the marketing and use of tar and pitch, as well as ammonia, that the substitution of by-product for bee-hive ovens can be expected to take place. Nevertheless, the by-product oven has already established itself, within the commercial limits thus imposed, as a thorough success in the economical production of the best grades of coke, and as time goes on there will undoubtedly ensue a large but gradual increase in its use.

PHYSICAL CHEMISTRY FOR ELECTRICAL ENGINEERS. By J. LIVINGSTON R. MORGAN, PH.D. 230 pp. New York: John Wiley & Sons. Price: $1.50.

This work is as compact a compilation of the conceptions now constituting physical chemistry as could be connectedly written. In the reviewer's opinion it is so condensed that the average engineer would find a little trouble in understanding it. The first chapter deals with fundamental principles, among which are included the author's decision to use in his book the term "combining weight, meaning by it that combining weight which is usually designated as the atomic weight," and "formula weight," instead of the "so-called molecular weight." This is to free the work from any conception of an hypothesis or inaccuracy. This laudable ambition has, in general, cost as much or more than it is worth. The common terms of the average physical chemist are the ones which the electrical engineer ought naturally to wish to learn.

The subject-matter is developed along the lines usually employed; A Consideration of the Laws of Gases, Energy and Its Laws, Solutions and Electrolytic Dissociation, Chemical Mechanics, Equilibrium and Electrochemistry. The choice of material considered under these different heads has been well made. No padding with useless commercial processes is visible. The book is a scientific treatise somewhat cramped for room. It may serve well when used in connection with a course of lectures or together with some more general work on the subject. A collection of 78 problems, with answers, completes the book. These problems are well selected to illustrate the most important laws of physical chemistry. W. R. WHITNEY.

PHYSICAL CHEMISTRY AND ITS APPLICATIONS IN MEDICAL AND BIOLOGICAL SCIENCE. By ALEX. FINDLAY, M.A., PH.D., D.Sc., Lecturer on Physical Chemistry, University of Birmingham. London, New York and Bombay: Longmans, Green & Co. 68 pages. Price, 75 cents.

The matter in this little book was presented to students interested in subjects related to medicine, in the form of lectures which were later printed in the *Birmingham Medical Review*. As they now appear in book form they afford a very readable exposition of the elementary principles of physical chemistry in non-mathematical treatment. The author has made a good selection of material and has given enough of fact and theory to satisfy the needs of many students whose work touches chemistry but incidentally. J. H. LONG.

RECENT PUBLICATIONS.

THE CYANIDE INDUSTRY THEORETICALLY AND PRACTICALLY CONSIDERED. By R. Robine and M. Lenglien. Translated by J. Arthur LeClerc with an appendix by C. E. Munroe. New York: J. Wiley & Sons. 1906. 11+408 pp. $4.00.

ELECTRIC FURNACES AND THEIR INDUSTRIAL APPLICATIONS. By J. Wright. New York: Norman W. Henley Pub. Co. 1905. 10+288 pp. $5.00.

URINARY ANALYSIS AND DIAGNOSIS BY MICROSCOPICAL EXAMINATION. By L. Heitzmann. Second edition. New York: W. Wood & Co. 1906. $2.50.

TEXT-BOOK OF PHARMACOLOGY. By A. R. Cushny. Fourth edition. London: Rebman. 1906. 17/6.

THIRD TREATISE ON THE EFFECTS OF BORAX AND BORIC ACID ON THE HUMAN SYSTEM. BEING A CRITICAL REVIEW OF THE REPORT OF DR. H. W. WILEY, CHIEF OF THE BUREAU OF CHEMISTRY OF THE U. S. DEPARTMENT OF AGRICULTURE. By O. Liebreich. London: Churchill. 1906. 78 pp. 5/.

THREE YEARS' COURSE OF PRACTICAL CHEMISTRY. By G. H. Martin. Third year. London: Rivingtons. 1906. 2/.

DIE STRUKTURFORMELN DER ORGANISCHEN CHEMIE MIT BERÜCKSICHT DER OFFIZINELLEN ORGANISCH-CHEMISCHEN PRÄPARATE DER PHARMAZIE UND DER MEDIZIN. By Max Biechele. Halle: C. A. Kaemmerer. 1906. 7+198 pp. Marks 3.

DIE CELLULOSEFABRIKATION (ZELLSTOFFFABRIKATION). PRAKTISCHE HANDBUCH FÜR PAPIER- UND- CELLULOSETECHNIKER. By Max Schubert. Third edition. Berlin: M. Krayn. 1906. 12+301 pp. Marks 6.

CONVERSATIONS ON CHEMISTRY. PART 1, FIRST STEPS IN CHEMISTRY. PART 2, CHEMISTRY OF THE MOST IMPORTANT ELEMENTS AND COMPOUNDS. By Wilhelm Ostwald. New York: J. Wiley & Sons. 1906. 8+373 pp. $2.00.

PRÉCIS DE DIAGNOSTIC CHIMIQUE MICROSCOPIQUE ET PARASITOLOGIQUE. By J. Guiart & L. Grimbert. Paris: F. R. de Rudeval. 900 pp. 15 fr.

PRACTICAL EXERCISES IN CHEMISTRY. By G. C. Donington. London: The Macmillan Co. 1906. 260 pp. 2/6.

RADIUM AND RADIO-ACTIVE SUBSTANCES: THEIR APPLICATION ESPECIALLY TO MEDICINE. By C. Baskerville. Philadelphia: Williams, Brown & Earle. 1905. 5+164 pp. $1.00.

NEW KNOWLEDGE. POPULAR ACCOUNT OF THE NEW PHYSICS AND THE NEW CHEMISTRY IN THEIR RELATION TO THE NEW THEORY OF MATTER. By R. Kennedy Duncan. New edition. London: Hodder & S. 1906. 284 pp. 6/.

LEHRBUCH DER CHEMISCHEN TECHNOLOGIE DER ENERGIEN. 1. BUCH. DIE CHEMISCHE TECHNOLOGIE DER WÄRME UND DER BRENNMATERIALEN. By Hanns von Jüptner. Wien: F. Deuticke. 1906. 5+256 pp. Marks 7.

ÜBER DIE VORGESCHICHTE UND DIE ANFÄNGE DER CHEMIE. EINE EINLEITUNG IN DIE GESCHICHTE DER CHEMIE DES ALTERTUMS. By Franz Strunz. Wien: F. Deuticke. 1906. 7+69 pp. Marks 2.

CANNING AND PRESERVING OF FOOD PRODUCTS WITH BACTERIOLOGICAL TECHNIQUE: A PRACTICAL AND SCIENTIFIC HANDBOOK FOR MANUFACTURERS OF FOOD PRODUCTS, BACTERIOLOGISTS, CHEMISTS, AND STUDENTS OF FOOD PROBLEMS. By E. Wiley Duckwall. Pittsburg: Pittsburg Printing Co. 1905. 478 pp. $5.00.

CHEMISTRY OF THE PROTEIDS. By Gustav Mann. New York: The Macmillan Co. 1906. 8+600 pp. $3.75.

LEHRBUCH DER CHEMIE FÜR TECHNISCHE ANSTALTEN. By Prof. Dr. Düsing. Kiel: R. Cordes. 1906. 6+116 pp. Marks 2.70.

ANORGANISCHE CHEMIE. By Ira Remsen. Third edition prepared by Dr. Karl Seubert. Tübingen: H. Laupp. 1906. 16+528 pp. Marks 9.40. (Bound, Marks 10-).

SYSTEMATIC INORGANIC CHEMISTRY. FROM THE STANDPOINT OF THE PERIODIC LAW. TEXT-BOOK FOR STUDENTS. By R. M. Caven and G. D. Lander. London: Blackie. 1906. 394 pp. 6/.

POLARISCOPE IN THE CHEMICAL LABORATORY. By G. W. Rolfe. London: The Macmillan Co. 1906. 8/.

METHODS OF ORGANIC ANALYSIS. By H. C. Sherman. London: The Macmillan Co. 1906. 7/6.

THE MICROSCOPY OF VEGETABLE FOODS WITH SPECIAL REFERENCE TO THE DETECTION OF ADULTERATION OF MIXTURES. By Andrew Lincoln Winton and Dr. Josef Moeller. New York: J. Wiley & Sons. 1906. 16+701 pp. $7.50.

The following bibliographies have been published by the Carnegie Library of Pittsburg. These are not intended to be complete but are rather lists of recent publications on the subjects which are mentioned. They will be sent to any one who desires them and who will send a stamp for postage.

Sodium Nitrate Industry of Chile.

Steam Turbines.

Malleable Castings.

Water Softening.